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IONIC SUSCEPTIBILITY OF BARIUM

By Mata Prasad, S. S. Dharmatti and C. R. Kanekar

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Recently several systematic investigations have been carried out to determine the ionic susceptibilities of several elements in their different valency states, from the molecular susceptibilities of their compounds. Hollens and Spencer[1] measured the susceptibilities of several compounds of cadmium and deduced therefrom the ionic susceptibility of cadmium. Bhatnagar and co-workers have carried out an extensive investigation on the determination of the ionic susceptibilities of various elements and they find that, generally, the experimentally deduced values are in fair agreement with those calculated theoretically by Slater's and Angus's methods. Bhatnagar and Bahl[2] studied salts of trivalent bismuth and deduced the ionic susceptibility of Bi^{+3}. Bhatnagar and Khanna[3] determined the ionic susceptibility of rubidium and Bhatnagar, Nevgi and Sharma[4] that of tin in di- and tetra-valent states. Trew[5] studied thallium compounds in different valency states to determine the ionic susceptibility of thallium. Nevgi[6] also studied thallium salts and found that his mean value for the thallium ion is less than that obtained by Trew. Bhatnagar, Nevgi and Ohiri[7] studied salts of mercury in mono- and di-valent states and deduced the ionic susceptibility of mercury which is in good agreement with the calculated values. Rao and Sriraman[8] have studied a number of salts both in solid and dissolved states and have determined the susceptibilities of ions like formate, acetate, nitrate, selenite and nitrite. They have pointed out the desirability of investigating compounds both in the solid and dissolved states, as they found slight changes in the ionic susceptibility values determined by the two methods.

The ionic susceptibility of barium calculated either by Slater's ($-33{\cdot}3\times10^{-6}$) or by Angus's ($-31{\cdot}51\times10^{-6}$) method is different from the experimental value given in the *International Critical Tables* ($-38{\cdot}2\times10^{-6}$). Hence the susceptibilities of a number of inorganic and organic salts of barium were measured and using the known values of the susceptibility of the various ions the susceptibility of barium ion was deduced therefrom.

Experimental

All substances used in this investigation were of extra pure quality. Some of them were Kahlbaum products while a few were obtained from Dr. Theodor Schuchardt. A few substances were prepared in the laboratory from extra pure chemicals. They were analysed quantitatively and only those substances which were found to be absolutely pure were employed for the purpose of investigation.

Barium carbonate was prepared by passing purified CO_2 through baryta water. Barium chromate, oxalate, tartarate and succinate were prepared by precipitation from a solution of Merck's extra pure barium chloride by the addition of the solution of ammonium salt of the corresponding acids. The formate, acetate, phthalate and salicylate were prepared by adding an excess of the corresponding acids to pure barium carbonate and crystallising them from solutions thus obtained. The crystals obtained were recrystallised thrice. The crystals of barium acetate were heated in a steam oven to get the anhydrous sample.

The Magnetic Balance employed and the procedure followed were the same as described by Prasad and Dharmatti.[12]

The results obtained are given in Tables I and II. In all cases the values obtained are the mean of three independent readings. Various values for the anions given by different workers have been utilised to deduce the ionic susceptibility of barium.

Discussion of Results

(*a*) *Salts of Inorganic Acids.*—The ionic susceptibilities of barium were calculated by the Slater's, Angus's and modified methods of Slater and Angus in the same manner as in the case of selenium (*cf.* Prasad and Dharmatti, *loc. cit.*). These values are given in Table III.

TABLE I

Barium Salts of Inorganic Acids

Substance	$-xa\times10^6$	$-xm\times10^6$	Values of other radicals $-x\times10^6$			$-x_{Ba^{+2}}\times10^6$	Mean $-x_{Ba^{+2}}\times10^6$
1. $BaCl_2\cdot2H_2O$	0·4070	99·42	H_2O	=	12·96		
			xCl'	=	23·1 (Hocart)	27·3	
				=	22·1 (Kido)	29·3	
				=	20·4 (Ikenmeyer)	32·7	
				=	20·1 (Pascal)	33·3	
				=	19·85 (Bhatnagar)	33·8	29·89
				=	20·0 (Sugden)	33·5	
				=	23·1 (Weiss)	27·3	
				=	24·1 (Pauling)	25·3	
				=	23·1 (Abonnene)	27·3	
				=	22·2 (Leiterer)	29·1	
2. $BaBr_2\cdot2H_2O$	0·3925	130·8	H_2O	=	12·96		
			xBr'	=	33·9 (Hocart)	37·08	
				=	34·7 (Kido)	35·48	
				=	34·8 (Ikenmeyer)	35·28	
				=	30·5 (Pascal)	43·88	
				=	32·5 (Reichender)	39·88	38·88
				=	31·4 (Farquharson)	42·08	
				=	31·0 (Sugden)	42·88	
				=	34·1 (Abonnene)	36·68	
				=	34·1 (Weiss)	36·68	
3. $Ba(NO_3)_2$	0·2513	65·69	xNO_3'	=	14·2 (Pascal)	37·29	
				=	20·1 (Kido)	25·49	
				=	18·0 (Sugden)	29·69	
				=	18·4 (Raychaudhari and Sengupta)	28·89	30·02
				=	18·2 (Pauling)	29·29	
				=	18·1 (Rao)	29·49	
4. $BaCO_3$	0·2847	56·20	xCO_3''	=	22·2 (Pascal)	34·0	
				=	28·1 (Kido)	28·1	29·37
				=	30·2 (Pauling)	26·0	

TABLE I—(*Contd.*)

Substance	$-x\alpha \times 10^6$	$-xm \times 10^6$	Values of other radicals $-x \times 10^6$	$-xBa^{+2} \times 10^6$	Mean $-xBa^{+2} \times 10^6$
5. $BaSO_4$	0·3062	71·44	xSO_4'' = 33·6 (Pascal)	37·84	
			= 39·0 (Kido)	32·44	33·64
			= 37·0 (Trew)	34·44	
			= 41·6 (Pauling)	29·84	
6. $BaSeO_4$	0·2113	59·29	$xSeO_4''$ = 23·89 (S)*	35·40	
			= 23·821 (A)	35·469	36·01
			= 22·74 (MS)	36·55	
			= 22·672 (MA)	36·618	
7. $Ba(ClO_3)_2, H_2O$ ..	0·3584	115·5	H_2O = 12·96		
			$xClO_3'$ = 25·8 (Trew)	50·94	
			= 30·2 (Kido)	42·14	47·87
			= 26·0 (Sugden)	50·54	
8. $BaCrO_4$	0·0501	12·7	$xCrO_4''$ = −21·86 (Bhatnagar, Prakash and Hamid's data)	34·56	
			= −35·2 (Trew)	47·9	42·72
			= −33·0 (Trew)	45·7	
9. $BaSeO_3$	0·2563	67·81	$xSeO_3''$ = 44·9 (Rao)	22·91	21·61
			= 47·5 (Kido)	20·31	

* Value for SeO_4'' has been computed by using the values for Se^{+6} calculated by Slater's method (S), Angus' method (A) and modified methods of Slater and Angus (Ms and MA) (*cf.* Prasad and Dharmatti, *Proc. Ind. Acad. Sci.*, 1940, **12**, 185).

TABLE II

Barium Salts of Organic Acids

Substance	$-xa \times 10^6$	$-xm \times 10^6$	Values of other radicals $-x \times 10^6$		$-xBa^{+2} \times 10^6$	Mean $-xBa^{+2} \times 10^6$
1. $(HCOO)_2Ba$	0·3250	73·7	$(HCOO)^-$	= 16·9 (Pascal's corrected data)	39·9	
				= 20·2 (Kido)	33·3	37·43
				= 17·3 (Rao)	39·1	
2. $(CH_3COO)_2Ba$ ..	0·3896	99·49	$(CH_3COO)^-$	= 28·9 (Pascal)	41·69	
				= 32·0 (Kido)	35·49	
				= 30·0 (Trew)	39·49	39·21
				= 30·0 (Hollens and Spencer)	39·49	
				= 29·8 (Rao)	39·89	
3. BaC_2O_4	0·2870	64·77	$C_2O_4)^{--}$	= 27·94 (Pascal's corrected data)	36·83	
				= 28·5 (Hollens and Spencer)	36·27	36·48
				= 28·44 (*Int. Crit. Tables*)	36·33	
4. $(CH_3COO)_2Ba$ ..	0·3851	97·59	$(CH_3COO)_2^{--}$	= 51·66 (Pascal's corrected data)	45·93	45·19
				= 53·14 (*Int. Crit. Tables*)	44·45	
5. $(CHOHCOO)_2Ba$ ..	0·4103	117·1	$(CHOHCOO)_2^{--}$	= 62·36 (*Int. Crit. Tables*)	54·74	
				= 63·8 (Trew)	53·3	54·75
				= 60·88 (Pascal's corrected data)	56·22	
6. $(C_6H_4COOHCOO)_2Ba, H_2O$	0·4621	224·3	H_2O	= 12·96		
			$(C_6H_4COOHCOO)^-$	= 83·11 (Pascal's corrected data)	45·12	42·34
				= 85·89 (*Int. Crit. Tables*)	39·56	
7. $(C_6H_4OHCOO)_2Ba, H_2O$	0·4681	201·0	H_2O	= 12·96		
			$(C_6H_4OHCOO)^-$	= 71·44 (Pascal's corrected data)	45·16	41·92
				= 74·68 (*Int. Crit. Tables*)	38·68	

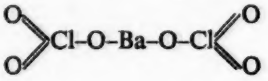
TABLE III

Calculated Ionic Susceptibilities of Divalent Barium

Slater's method ($-\chi \times 10^6$)	Angus's method ($-\chi \times 10^6$)	Modified method of Slater ($-\chi \times 10^6$)	Modified method of Angus ($-\chi \times 10^6$)
33·3	31·51	37·90	34·16

It will be noticed from Table I that except in the case of chlorate, chromate and selenite, the mean ionic susceptibility of barium deduced from all other salts is in good agreement with the calculated values. These discrepancies have been examined critically in the following:—

(1) The value for the chlorate ion was calculated in the manner similar to the one followed by Gray and Farquharson,[9] representing the barium chlorate as:



Slater's value for double bond oxygen, and (i) Gray and Farquharson's value for Cl^{+5} ($-5{\cdot}71 \times 10^{-6}$) and (ii) Slater's value for Cl^{+5} ($-4{\cdot}49 \times 10^{-6}$) were used. The ionic susceptibilities of barium deduced by subtracting these values for the chlorate ion from the experimental molecular susceptibility of barium chlorate are shown in Table IV.

TABLE IV

$-\chi m \times 10^6$ of $Ba(ClO_3)_2$, H_2O	Values of other radicals ($-\chi \times 10^6$)	$-\chi Ba^{+2} \times 10^6$
115·5	χ_{H_2O} = 12·96 (i) $\chi_{ClO_3'}$ = 36·62 (ii) „ = 35·4	29·30 31·74

The ionic susceptibility of barium thus obtained agrees fairly well with the calculated values. The agreement is very good with the value ($-31{\cdot}51 \times 10^{-6}$) calculated by Angus's method when Slater's value for Cl^{+5} is used.

(2) The value for the chromate ion if calculated from the molecular susceptibility of silver chromate observed by Bhatnagar, Prakash and Hamid[10] by subtracting from it the value for two silver ions ($\chi_{Ag}{}^{+1} = -31{\cdot}0 \times 10^{-6}$;

cf. *International Critical Tables*) comes out to be $+ 21{\cdot}86 \times 10^{-6}$. The value for the ionic susceptibility of barium obtained by using this value for chromate ion is in good agreement with the theoretically calculated values. The use of the other two values for chromate ion given by Trew, gives very high values for the ionic susceptibility of barium and hence the mean of all the values is also considerably high. One of the values ($- 33{\cdot}0 \times 10^{-6}$) given by Trew does need modification. This value has been obtained by subtracting the ionic value for potassium ($- 18{\cdot}5 \times 10^{-6}$; cf. *International Critical Tables*) from the observed molecular susceptibility of K_2CrO_4. This value for potassium ion is higher than the value calculated by Slater's method ($- 14{\cdot}43 \times 10^{-6}$), and is even higher than the experimentally obtained values of Pascal and Pauling ($-14{\cdot}5 \times 10^{-6}$), Stoner ($- 13{\cdot}4 \times 10^{-6}$), Joos ($- 14{\cdot}5 \times 10^{-6}$), Ikenmeyer ($- 16{\cdot}9 \times 10^{-6}$), Abonnene ($- 16{\cdot}3 \times 10^{-6}$) and Brindley ($- 13{\cdot}5 \times 10^{-6}$), most of which are nearly the same as the Slater's calculated value. If a mean of all the experimental values ($- 14{\cdot}83 \times 10^{-6}$) is used for potassium ion, the ionic susceptibility for chromate ion comes out to be $+ 25{\cdot}7 \times 10^{-6}$, which is nearly the same as the one obtained by Bhatnagar, Prakash and Hamid.

The susceptibilities of barium ion obtained by using these values of chromate ions are shown in Table V.

TABLE V

Substance	$-x_m \times 10^6$	$-x \times 10^6$ for cations	$-x_{CrO_4^{--}} \times 10^6$	$-x_{Ba^{++}} \times 10^6$	Mean $-x_{Ba^{++}} \times 10^6$
K_2CrO_4 ..	4·00	14·85	− 25·70	38·40	36·48
Ag_2CrO_4 ..	40·14	31·00	− 21·86	34·56	

The mean value thus obtained is in fair agreement with the values calculated by Slater's and Angus's methods.

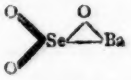
(3) The discrepancy in the case of selenite may be due to the very high values of selenite ion given by Kido[11] and Rao.[8] Prasad and Dharmatti[12] who studied silver selenite and selenious acid have found that susceptibilities of these substances calculated from Kido's and Rao's data are higher than the experimental values. The values for the selenite ion were, therefore, calculated from the susceptibilities of silver selenite and selenious acids and from those of sodium, ammonium and zinc selenite which have been investigated in this laboratory and they were used in deducing the ionic susceptibility of barium. The results obtained are shown in Table VI.

TABLE VI

Substance	$-\chi m \times 10^6$	$-\chi \times 10^6$ for cations	$-\chi SeO_3'' \times 10^6$	Mean $-\chi SeO_3'' \times 10^6$	$-\chi Ba^{+2} \times 10^6$
H_2SeO_3 ..	45·45	H = 3·05 (*Int. Crit. Tables*)	39·35	39·47	28·34
		= 2·93 (Pascal's corrected data)	39·59		
Ag_2SeO_3 ..	102·2	Ag = 31·0 (*Int. Crit. Tables*)	40·2	40·20	27·61
$(NH_4)_2SeO_3$ ..	68·74	NH_4 = 12·0 (Stoner)	44·74		
		= 12·4 (Kido)	43·94	39·14	28·67
		= 20·0 (Sugden)	28·74		
Na_2SeO_3	58·45	Na = 5·4 (Abonneve)	47·65		
		= 7·0 (Kido)	44·45		
		= 7·6 ,,	43·25		
		= 9·2 (*Int. Crit. Tables*)	40·05		
		= 5·2 (Brindley)	48·05	43·83	23·98
		= 8·0 (Weiss)	42·45		
		= 10·4 (Ikenmeyer)	37·65		
		= 6·1 (Hoare and Brindley)	46·25		
		= 6·9 (Flordal and Frivold)	44·65		
$ZnSeO_3$ ..	54·23	Zn = 13·5	40·73		27·08

Mean $-\chi Ba^{+2} \times 10^6 = 27·14$

Thus the mean value obtained for barium ion is lower than the value calculated by Angus's method but it is in better agreement with the theoretical value than the value given in Table I. The low value of the ionic susceptibility is probably due to the tight-binding of barium in barium selenite as can be seen from its constitution.



The results for barium salts of inorganic acids have been summarised in Table VII in which these salts have been arranged in the order of increasing number of electrons. Column 3 gives their observed susceptibilities, and column 4 gives the mean values for the ionic susceptibility of barium as modified according to the discussion in the foregoing pages. The last column gives the mean of all the values, which is fairly in good agreement with the values calculated by Angus's method.

TABLE VII

Substance	No. of electrons N_m	$-\chi m \times 10^6$	$-\chi Ba^{+2} \times 10^6$	Mean $-\chi Ba^{+2} \times 10^6$
1. $BaCO_3$	86	56·20	29·37	
2. $BaSO_4$	104	71·44	33·64	
3. $BaCl_2 2H_2O$	110	99·42	29·89	
4. $BaCrO_4$	112	12·70	36·48	
5. $BaSeO_3$	114	67·81	27·14	32·30
6. $Ba(NO_3)_2$	118	65·69	30·03	
7. $BaSeO_4$	122	59·29	36·01	
8. $BaBr_2 2H_2O$	146	130·80	38·88	
9. $Ba(ClO_3)_2 \cdot H_2O$	148	115·50	29·30	

Ikenmeyer[13] has studied the halides of alkali and alkaline earth metals in solution and finds that the molecular susceptibility is a linear function of the sum of the nuclear charges of the atoms constituting the molecules,

$$-\chi_m = C_1 N_m + C_2$$

where N_m is the sum of the electrons in the compound, $C_1 = 0{\cdot}803 \times 10^{-6}$ and C_2 is another constant specific for a given series of salts. Trew (*loc. cit.*) found that this relation generally holds in the case of thallous salts, though there are some marked deviations. He finds $C_1 = 0{\cdot}7 \times 10^{-6}$ and $C_2 = -17 \times 10^{-6}$. An application of this relation to the case of barium salts of inorganic acids showed that the various points on $-\chi_m$ and N_m graph do not lie on a straight line; only points corresponding to (i) barium halides and (ii) barium carbonate, sulphate and chlorate lie on two separate straight lines; the values for C_1 and C_2 for the two straight lines being $0{\cdot}87 \times 10^{-6}$ and $+3{\cdot}7 \times 10^{-6}$ in the first case and $1{\cdot}0 \times 10^{-6}$ and $-32{\cdot}5 \times 10^{-6}$ in the second. The two values of C_1 are in fair agreements with each other and with the value found by Ikenmeyer.

Ikenmeyer also found that the susceptibility of an ion is given by the relation

$$-\chi_{ion} = C_1 Z + C_2'$$

where Z is the number of electrons in the ion and C_2 is another constant ($-5{\cdot}1 \times 10^{-6}$) in the case of the alkaline-earth ions. If the value of the ionic susceptibility of barium obtained experimentally from the inorganic salts and the two values of C_1 are used in the above equation, the values of C_2' come out to be $-14{\cdot}68 \times 10^{-6}$ and $-21{\cdot}7 \times 10^{-6}$ respectively. These are far different from the one obtained by Ikenmeyer.

The radius of barium ion was calculated from its mean ionic susceptibility ($-32{\cdot}30 \times 10^{-6}$) by the method adopted by Trew (*ibid.*) and was

found to be 1·61 Å. The value observed by Wassastjerna for the ionic radius of barium is 1·40 Å.

(*b*) *Barium Salts of Organic Acids.*—Barium salts of organic acids have been arranged in the order of increasing number of electrons, in Table VIII, which gives the molecular susceptibilities (column 4) and the ionic susceptibilities of barium (column 5), obtained from these salts (*cf.* Table II).

TABLE VIII

Substance	N	No. of carbon atoms	$-\chi m \times 10^6$	$-\chi Ba^{+2} \times 10^6$	Mean $-\chi Ba^{+2} \times 10^6$
1. BaC_2O_4	100	2	64·77	36·48	
2. $(HCOO)_2Ba$	102	2	73·70	37·43	
3. $(CH_3COO)_2Ba$ ..	116	4	97·59	45·19	
4. $(CH_3COO)_2Ba$ ..	118	4	99·49	39·21	42·47
5. $(CHOHCOO)_2Ba$ ..	132	4	117·1	54·75	
6. $(C_6H_4OHCOO)_2Ba$ ..	208	14	201·0	41·92	
7. $(C_6H_4COOHCOO)_2Ba$, H_2O	236	17	224·3	42·34	

The susceptibility of barium formate and acetate [$(CH_3COO)_2Ba$, H_2O] have also been determined by Rao and Sriraman[8] and the values for their molecular susceptibilities are, respectively, $-66·6 \times 10^{-6}$ and $-100·1 \times 10^{-6}$. It will be seen from the above table, that the values found by the authors are higher than those found by Rao and Sriraman.

A study of the above table shows that the mean ionic susceptibility of barium ($-42·47 \times 10^{-6}$) obtained from these salts is considerably higher than the values calculated by Slater's and Angus's methods and that obtained from barium salts of inorganic acids. Similar observations have been made by Trew (*loc. cit.*) in the case of the thallium salts. The increase in the ionic susceptibility can be attributed either to the bond effects in the compound or to the increase in the size of the ionic radius. As the increase due to the bond effects has been taken into account in calculating the values for the anions according to Pascal's data, it seems that the increase in the ionic susceptibility is mostly due to the second cause. This may be evidenced by the fact that the increase in the ionic susceptibility is roughly followed by an increase in the number of carbon atoms. The last-named observation was also made by Trew.

Nevgi (*loc. cit.*) holds that the high value obtained by Trew, for the ionic susceptibility of thallium, is due to the use of merely Pascal's data which will not be applicable to heteropolar salts as the data is based upon the investigation of homopolar compounds. In the case of barium formate,

acetate and oxalate, all the possible values for the anions have been used and it is found that even in these cases the ionic susceptibilities are higher than the calculated values. In the case of the oxalate, the susceptibility of the oxalate ion was determined from the susceptibilities of heteropolar oxalates and this value was employed in deducing the ionic susceptibility of barium. These calculations are shown in Table X.

TABLE X

Substance	$-xm \times 10^6$	Value of other ions ($-x \times 10^6$)	$-x(C_2O_4)^{--} \times 10^6$	$-x Ba^{++} \times 10^6$	Mean $-x Ba^{++} \times 10^6$
CdC_2O_4 ..	53·13	24·85	28·28	36·49	33·33
$Tl_2C_2O_4$ ..	109·4	37·4	34·6	30·17	

The mean value for the ionic susceptibility of barium given above is almost the same as the one calculated by the Slater's method. However, the data for the deduction of the value for the oxalate ion is too meagre to arrive at a definite conclusion.

It might also be suggested that the high values for the barium ion obtained in the case of the salts of organic acids may also be due to the change in the electronic configuration of — O—bond. Consequently Pascal's value ($-4{\cdot}61 \times 10^{-6}$) used for organic compounds for this bond may not be applicable in the case of ionic salts. Further work in connection with this point is in progress.

From the mean ionic susceptibility of barium obtained from organic salts, the ionic radius of barium has been calculated and is found to be 1·849 Å, which is higher than (1) the one obtained from the barium value deduced from the salts of inorganic acids (1·61 Å) and (2) the one found by Wassastjerna (1·40 Å) by the X-ray method.

Summary

The susceptibilities of a number of barium salts of inorganic and organic acids have been determined by Guoy's Balance and using all possible available values for the anions, the ionic susceptibility of barium has been calculated. In the case of salts of inorganic acids the mean ionic susceptibility of barium agrees well with the values theoretically calculated by Slater's and Angus's methods. The mean value deduced from the salts of organic acids is found to be higher than the calculated value and that found from inorganic salts. The probable reasons have been discussed in detail. It has been suggested that the values of several anions need revision.

The ionic radius of barium has also been calculated and has been compared with the value observed by Wassastjerna.

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KANUGIN, A CRYSTALLINE COMPONENT OF THE ROOTS OF *PONGAMIA GLABRA*

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OF the different parts of *Pongamia glabra*, the seeds and the fixed oil derived from them are well known for their medicinal properties. Two crystalline compounds responsible for these properties have so far been isolated. The constitution of one of them, karanjin, has been definitely established and it has been obtained by synthesis also.[1] The other compound known as pongamol was only recently discovered and its study is still incomplete.[2] Various other parts of the tree have also been used for medicinal purposes in India from very early times. Among them the roots seem to possess antiseptic properties. The juice obtained from them has been used for cleansing foul ulcers and closing fistulous sores and is given internally in gonorrhea and urethritis. They have therefore been examined and some of the results are reported in this communication.

A preliminary extraction of the powdered roots with alcohol gave a highly coloured extract which yielded a dark residue on concentration. It showed no tendency to crystallise. However, by extracting it with ligroin much of the coloured matter was left behind and from the solution a poor yield of a colourless crystalline solid was obtained with difficulty. When, however, the material was directly extracted with hot ligroin (*b.p.* 90–110°) the extract was much less coloured. On concentration and treatment with a little ether in order to remove resins and oily matter a mass of almost colourless crystalline solid was obtained. Subsequent extraction of the root powder with alcohol did not yield any definite component. Hence the study of this extract was not made in any detail. Comparative experiments using the entire root and the root bark alone indicated that the above-mentioned crystalline substance was present mostly in the bark. Consequently in all the later experiments this part of the root alone has been employed.

The crystalline compound obtained from the ligroin extract can be easily recrystallised from alcohol-acetic acid mixture and thus rendered pure. It melts at 197–8° and has the molecular formula $C_{19}H_{18}O_7$. It

seems to differ from all known substances. It is definitely different from karanjin and pongamol. It has therefore been given the new name " kanugin " derived from the Telugu name of the tree 'Kanuga'. Derivations from the botanical name of the tree *Pongamia glabra* and the Sanskrit name ' karanja ' are already in use, in the case of pongamol, glabrin (the nitrogenous compound present in the seeds)[3] and karanjin.

Kanugin is a neutral substance. Since it is insoluble in alkali and gives no colouration with ferric chloride or lead acetate it may not contain any phenolic hydroxyl groups. It however has three methoxyl groups in the molecule and seems to be a completely methylated compound. In this respect it resembles rotenone the chief active principle of the roots of another leguminous plant *Derris elliptica*. However, it does not show the usual rotenone colour reactions. On the other hand it gives a deep red colour by reduction with magnesium and hydrochloric acid thus showing that it belongs to the group of methoxy-flavones.

It is highly significant that while the seed contains a good amount of karanjin and some pongamol, they are absent from the root. It happens not infrequently that the same compound is present in different parts of the same plant though in varying amounts. This is obviously not the case in *Pongamia glabra*. The characteristic differences between the crystalline components of the seed and of the root are given in the following table. However, all the concerned compounds seem to be flavone derivatives.

	Karanjin	Pongamol	Kanugin
M.p.	158°	128°	197°
Mol. formula	$C_{18}H_{12}O_4$	$C_{18}H_{14}O_4$	$C_{19}H_{18}O_7$
Conc. H_2SO_4	Pale yellow soln.; green after 20 min. bluish green after 40 min.	Yellow soln. with green fluorescence ; deep emerald green in 5 min.	Yellow soln. with green fluorescence ; orange after 10 min. and red after half an hour.
$FeCl_3$ colour	Nil	Deep red	Nil
Dil. aq. NaOH	Insoluble	Almost insoluble	Insoluble
Methoxyl	Present	Present	Present
Reduction with Mg+HCl ..	Orange yellow	Orange red	Deep red
Boric-citric reaction ..	Negative	Positive	Positive
Taste	Slightly bitter	Less bitter	Not bitter

Experimental

The sample of the roots was obtained from the trees in the Andhra University campus in March. The roots from younger trees were about ½–1 inch in diameter and were more easily available near the ground surface. The more mature trees yielded roots varying in thickness from

1 to 3 inches. The bigger roots were more easily available in bulk and provided bark more easily. However, no selection was made of the material and it was a composite sample from roots of different sizes. After washing the roots free from soil, the bark was separated from the inner woody portion, dried and powdered.

Extraction with alcohol.—The powdered bark was extracted for ten hours with boiling alcohol. The extract was poured off and a second extraction was made using fresh alcohol for six hours. The combined extract was concentrated by distilling on a water-bath as far as possible and allowed to stand. Since no solid separated even after a number of days, the solution was evaporated from a porcelain basin on a steam-bath and the residue finally dried in a steam oven. The dark pitch-like residue was then extracted with boiling ligroin and the extract which was pale brown in colour evaporated to dryness. The residue was dissolved in alcohol and diluted with ether. On slow and spontaneous evaporation of this solution a light granular solid gradually separated out along with some resin. It was filtered, washed with ether and crystallised from alcohol containing a few drops of acetic acid. Clusters of colourless needles melting at 187° with a little previous sintering were obtained. After one more recrystallisation the melting point rose to 194–95°.

Extraction with ligroin.—The powdered root bark was extracted with hot ligroin three times, heating on a steam-bath for 10, 6 and 6 hours using fresh solvent for each operation. The combined extract was concentrated as far as possible on an oil-bath maintained at 100–10°. The residual dark and viscid liquid (about 100 c.c. from 2 kg. of the powder) was treated with ether (100 c.c.) and crystallisation induced by stirring vigorously with a glass rod and scratching the sides of the flask. A considerable amount of granular solid was formed within about half an hour. After allowing to stand further for three hours it was filtered and washed with ether in order to remove adhering oily and resinous impurities. Crystallisation from alcohol-acetic acid mixture yielded a colourless solid melting at 192° and sintering a few degrees earlier. A second crystallisation from the same solvent gave pure kanugin in the form of fine needles and narrow rectangular plates melting at 197–98°. Further crystallisations did not raise the melting point. The yield of the pure substance was about 0·05% on the weight of the dry bark powder. (Found: C, 63·7; H, 4·7; OCH_3, 25·6; $C_{19}H_{18}O_7$ requires C, 63·7; H, 5·0; OCH_3 (3), 26·0%. Molecular weight determined by Rast's method : 360, 341 ; $C_{19}H_{18}O_7$ requires mol. wt. 358.)

The compound was sparingly soluble in alcohol and moderately soluble in acetic acid. It was insoluble in dilute aqueous alkali by which it was unaffected even after boiling for 10 minutes. An alcoholic solution gave no colour with ferric chloride or lead acetate. It dissolved in cold concentrated sulphuric acid giving a yellow solution with a faint green fluorescence; the solution turned green after keeping for about 5 minutes, orange after 10 minutes and red after half an hour, the fluorescence becoming less and less apparent. Concentrated hydrochloric acid dissolved the compound producing a yellow solution. On reduction of the alcoholic solution with magnesium powder and hydrochloric acid a bright red colour was produced. A positive result was obtained with Wilson's boric acid test. Kanugin was compared with rotenone using the following reactions:

(1) A small quantity of kanugin was placed on a porcelain bit and a drop of concentrated nitric acid added. The substance was partly charred and the rest dissolved to give a yellow solution. On treating this with a few drops of ammonia no change in colour was observed. Rotenone gives a red solution with nitric acid and the solution turns green or bluish green with ammonia.

(2) A chloroform solution of kanugin (about 2 mg. in 5 c.c.) was mixed with a chloroform solution of thymol (5 c.c. of a 10% solution) and subsequently treated with a few c.c. of concentrated hydrochloric acid containing a trace of nitric acid and well shaken. The chloroform layer was coloured yellow which turned dirty brown after about half an hour. Rotenone gives an olive or bluish green colour in a few minutes.

Summary

A crystalline compound melting at 197–8° and having the molecular formula $C_{19}H_{18}O_7$ has been isolated from the roots of *Pongamia glabra*. It has been named kanugin. It is a neutral body having three methoxyl groups and it differs in its properties from karanjin, pongamol and rotenone.

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PIGMENTS OF THE FLOWERS OF *HIBISCUS SABDARIFFA*

Isolation of Sabdaretin, a New Hydroxyflavone

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In a recent publication of ours,[1] the isolation of hibiscitrin, a glycoside of hibiscetin was described, and the constitution of the aglycone was established as 3 : 5 : 7 : 8 : 3′ : 4′ : 5′-heptahydroxyflavone. This flavonol was originally prepared along with gossypetin by Perkin[2] who employed as his starting material the entire flowers of *Hibiscus sabdariffa*, consisting of stalk, calyx, epicalyx and corolla. The deep red calyx was later examined by Yamamoto and Osina[3] who isolated therefrom an anthocyanin named hibiscin which was shown to be a delphinidin derivative. A careful analysis of the calyx and the associated parts such as the epicalyxhas now shown that they contain very little of anthoxanthins. Hence it is clear that the petals alone are responsible for the anthoxanthin pigments. Consequently we have now made a detailed examination of a pure sample of the flower petals, and the results are presented in this paper.

The procedure followed runs practically on the same lines as described in our previous publications relating to cotton and other flowers. When an alcoholic extract of the petals is concentrated and allowed to stand for a long time, hibiscitrin gradually separates out (Fraction I). After the distillation of the alcohol from the mother-liquor, the material is taken up with water. Ether-extraction of this solution gives no crystalline product. But the aqueous solution deposits a solid which is collected in two fractions (II and III) and these are shown to be hibiscitrin and gossypitrin respectively. The neutral lead acetate precipitate yields a new compound called sabdaritrin, while the basic lead acetate fraction is too small to be studied.

Sabdaritrin has the formula $C_{21}H_{20}O_{14}$, $3H_2O$ and melts at 251–53° (decomp.). On boiling with dilute sulphuric acid, it yields a yellow crystalline substance named sabdaretin. The latter has the formula $C_{15}H_{10}O_8$,

$3H_2O$ and does not melt below 350°. It gives prominent colour changes with alkaline buffer solutions, a red colour when reduced with magnesium and hydrochloric acid, and a red precipitate with lead acetate, and so it is considered to be most probably a flavonol. On acetylation, it produces an acetyl derivative melting at 198–200°.

Besides the analytical results, sabdaritrin differs markedly in many of its properties from both gossypitrin and hibiscitrin with which it is occurring side by side in the flowers. The two latter have several points in common. They dissolve in dilute alkali to form green solutions which change to blue in a moment and further to greenish blue on shaking with air, whereas sabdaritrin forms first a yellow solution which rapidly changes to purple red and fades to reddish brown in a few minutes. With alkaline buffer solutions, gossypitrin and hibiscitrin give emerald green as the characteristic coloration whereas the new compound does not produce any green but yields crimson as the prominent colour. Hibiscetin and gossypetin similarly differ from sabdaretin. The former two produce green and blue as the prominent colours with alkaline buffer solutions; on the other hand, sabdaretin gives only a green and no blue colour. It may also be noted that hibiscitrin, gossypitrin and their aglycones are sensitive to alkaline buffer solutions of even the lower range (10·4 and 11·0) whereas sabdaritrin and sabdaretin respond only at the higher range (12·8 and 13·4).

The flower petals of *Hibiscus sabdariffa* contain, therefore, three definite compounds, hibiscitrin, gossypitrin and sabdaritrin belonging to the anthoxanthin group. This is in sharp contrast to the allied flowers of *Hibiscus cannabinus* from which only cannabiscitrin accompanied by a little of its aglycone could be obtained. A small-scale study of the anthocyanins present in the deep red central spots of the petals of *Hibiscus sabdariffa*, according to the method of Robinson and co-workers, has shown that it is a delphinidin derivative resembling hibiscin present in the calyx.

A more detailed study of sabdaritrin and sabdaretin could not be made due to lack of material and it will be undertaken as early as possible.

Experimental

Fraction I. Hibiscitrin:

The dried petals were extracted with boiling methylated spirits, and the combined alcoholic extract was concentrated to small bulk. After removing the wax and resin that had separated out, by filtration through fluted filters, the clear concentrate was allowed to stand. A yellow solid began to appear in about a month, and the deposition seemed to be complete at

the end of three months. The solid was filtered and washed well with water till it assumed a lemon-yellow colour. It was however, not pure and was sticky to the touch. Therefore a solution of it in a small quantity of pyridine was diluted with water till the impurities began to separate in a colloidal form. They were completely precipitated by the addition of a little calcium chloride and filtered. On concentrating the clear filtrate to small bulk, hibiscitrin crystallised out. After one more crystallisation from alcohol it appeared as yellow rectangular plates. On heating, it sintered at about 225°, became a semifluid a few degrees higher and decomposed at 238–40°. A yield of 6 g. was obtained from 1 kg. only and not from 3 kg. of the petals as mentioned in our former publication.[1]

Fractions II and III. Hibiscitrin and Gossypitrin:

The alcoholic mother-liquor left after the removal of Fraction I was diluted with a large volume of water, and the alcohol was removed almost completely by heating on a water-bath. After filtering off the resins that had separated out and concentrating to small bulk, the clear solution was extracted with ether and allowed to stand. The ether extract did not yield any pigment, but from the aqueous solution a yellow substance crystallised out within two or three days. After one crystallisation from alcohol, this substance also sintered at about 225°, became semifluid a few degrees higher and decomposed at 238–40°. It was therefore identified as hibiscitrin and this was confirmed by hydrolysis when it yielded an aglycone which melted at about 350° (decomp.) and gave an acetyl derivative identical with acetyl hibiscetin melting at 242–44°. After fifteen days some more pigment separated out from the aqueous solution. It was filtered, washed well with water and crystallised from glacial acetic acid, when it appeared as yellow needles. It was different from the glycoside, hibiscitrin, since it melted at 250–52° (decomp.) and produced an acetyl derivative melting at 242–44°. It was identified as gossypitrin from a study of its colour reactions with buffer solutions and a comparison of its acetyl derivative with acetyl gossypitrin. In this fraction hibiscitrin and gossypitrin were isolated in an yield of 2 g. and 1 g. respectively from 1 kg. of the petals.

Neutral Lead Acetate Fraction—Sabdaritrin:

The mother-liquor left after removing Fractions II and III, was treated with lead acetate solution when a brownish red precipitate was formed. It was filtered, suspended in water and decomposed in the usual way with hydrogen sulphide. The aqueous solution thereby obtained was concentrated and left aside. After nearly four months, some yellowish brown solid was deposited. It was filtered and purified by crystallisation from

aqueous pyridine. It appeared as yellow rectangular plates swelling and decomposing at 251–53° with sintering a few degrees earlier. (Found in the air-dried sample: C, 45·3; H, 4·8; $C_{21}H_{20}O_{14}$, $3H_2O$ requries: C, 45·8; H, 4·7%.) It was sparingly soluble in water, alcohol and even acetic acid but it freely dissolved in pyridine. When treated with ferric chloride, its alcoholic solution gave a brownish green colour, and with sodium hydroxide, it immediately assumed a yellow colour which later changed to brownish red, then red, then scarlet red and finally purple red. After five minutes the colour was reddish brown.

Sabdaretin :

(*a*) *Preparation.*—The new pigment, sabdaritrin (0·5 g.) was boiled under reflux with 7% sulphuric acid (50 c.c.). During the course of half an hour the substance went completely into solution, and no fresh solid separated out even after one hour. After boiling for two hours, the solution was filtered hot in order to remove some extraneous impurities and cooled when sabdaretin crystallised out as shining golden yellow needles. It was subsequently recrystallised from boiling water. (Found in the air-dried sample: C, 45·8; H, 3·5; $C_{15}H_{10}O_9$, $3H_2O$ requires C, 46·4; H, 4·1%.)

(*b*) *Properties.*—This substance, unlike sabdaritrin, was freely soluble in boiling water and could be conveniently crystallised from it. It was easily soluble in alcohol, acetic acid and also pyridine. When its aqueous or alcoholic solution was treated with a drop of alkali, immediately a brownish red colour developed. With ferric chloride a brownish red colour and with lead acetate a deep red precipitate were produced. On heating, the substance shrank and became dark at about 300° but did not melt even at 360°. When boiled with acetic anhydride and anhydrous sodium acetate, it formed the acetyl derivative which could not, however, be easily crystallised. On boiling with the ordinary solvents like alcohol and acetic acid, it seemed to undergo some decomposition and assumed a sticky resinous form. It was, therefore, dissolved in a small amount of acetic anhydride and the clear solution was treated with some absolute alcohol. From this mixture the substance crystallised during the course of two days as colourless long narrow rectangular plates which sintered at about 160° and melted at 198–200° (decomp.).

Colour Reactions of Sabdaritrin and Sabdaretin with Alkaline Buffer Solutions

pH	Sabdaritrin	Sabdaretin
8·6	Slowly dissolved to form pale yellow solution	Readily dissolved to give deep golden yellow solution, which became brown in 3 minutes and faded gradually within 15 minutes
9·2	More ready dissolution, and the solution was deep yellow	Same changes as above, the brown appearing within a minute
10·4	Same behaviour as the above	Deep golden yellow solution with a brownish tinge (½ minute)
11·0	Do.	Immediate yellow solution which became yellowish brown on shaking
11·6	Do.	The yellow was visible only for a moment and then changed to brown
12·2	Deep yellow solution which became crimson red within 3 minutes	Quick succession of changes :— Yelow solution, yellowish brown (shaking), dull green (½ min.), emerald green (1 min.), brownish yellow (1½ min.), yellowish brown (2 min.)
12·8	Yellow solution, brownish yellow (½ min.), brownish red (1 min.), crimson red (2 min.)	Same changes as above but very rapid :— Golden yellow, brown, green (½ min.), brown (1 min.). The green and brown were alternating for some time on shaking with air. The solution became completely brown in an hour
13·4	Same changes as the above but more quickly	Same changes as the above but more rapidly, the green following the yellow almost immediately

After 24 hours the colour was yellowish brown in the case of sabdaritrin and light brown with sabdaretin solutions.

Summary

The flower petals of *Hibiscus sabdariffa* contain hibiscitrin as the main component. Gossypitrin is present to a smaller extent. Besides these two, a small amount of a new compound named sabdaritrin has also been isolated. On boiling with dilute sulphuric acid it yields a new hydroxyflavone called sabdaretin.

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CHEMICAL EXAMINATION OF THE SEEDS OF *ALANGIUM LAMARKI*, THWAITES

Isolation of Alangol

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Alangium Lamarki, Thwaites, known in Hindi as "Akola" and in Sanskrit and Bengali as "Ankula" is a small handsome evergreen tree belonging to the Natural Order Cornaceæ. It grows quite well in the sub-Himalayan tract and also in Central and Southern India. The seeds of the plant are highly medicinal and have been described by Kirtikar and Basu[1] as cooling, tonic, nutritive and useful in the case of burning sensation in the body and also in consumption and hæmorrhage. They have also a reputation in the cure of leprosy. Besides the seeds, the bark and the root of the plant have highly medicinal properties, but they will be the subject of a future communication.

The raw fruits have a deep crimson pericarp which on drying assumes a dark-brown, in fact almost black colour. The dried seeds are 10–15 mm. in length and 5–8 mm. in diameter and are not unlike small hazelnuts in appearance. On breaking off the outer shell, the inner kernel is found to be white or pale cream coloured, very closely resembling the kernel of groundnut, but having a peculiar characteristic smell of the drug.

The most surprising fact about the seeds is that they do not contain any appreciable quantity of fixed oil. On extraction of the crushed kernels with benzene, a colourless crystalline substance having all the properties of a sterol is ultimately obtained, melting at 296° C. This substance has consequently been named "alangol". The molecular formula of this compound from the analytical data and its molecular weight by Rast's method has been found to be $C_{42}H_{84}O_7$. From the formula and also its very high melting point, it is undoubtedly the most complicated sterol that has yet been discovered. The substance has been found to contain an alcoholic hydroxy group, since it yields a monoacetyl, a monobenzoyl and a monophenyl urethane derivative respectively on treatment with acetic anhydride, benzoyl chloride and phenylisocyanate. About the nature of the remaining six atoms of oxygen in the molecule, no indication has as yet been found. A digitonide of the sterol has also been prepared.

Alangol is present in the seeds of *Alangium Lamarki* to the extent of 0·05 per cent. (0·08 per cent. of the kernels). The kernels of the seeds besides containing alangol, also contain a large proportion of starch, small amounts of sugars, tannins, traces of protein matter, but no alkaloids, glucosides, fats or bitter principles. Fully mature and ripe seeds have been found to contain a much greater proportion of alangol than unripe or immature seeds. It is interesting to note in this connection that in the Ayurvedic system of medicine, only the ripe seeds have been prescribed.

The pericarp or shells of the seeds have also been examined. They have been found to contain nothing that is interesting from the chemical point of view. They only contain tannins, sugars and colouring matters besides cellulose and inorganic substances.

Experimental

Shells and kernels of the seeds.—10 kilos of the authentic ripe seeds were procured from the Punjab Ayurvedic Pharmacy, Amritsar, and the kernels extracted from them by the laborious process of shelling and picking. The kernels weighed 71·4 per cent. of the whole seeds, the remainder being the shells. Both shells and kernels on incineration left a greyish-white ash, which was analysed qualitatively with the following results:

Shell ash (8·5%).—Water-soluble portion (56·3%) contains chloride, sulphate, carbonate, sodium and potassium. Water-insoluble portion (43·7%) contains calcium, magnesium, silica, alumina, iron and phosphate.

Kernel ash (3·03%).—Water-soluble portion (76·9%) contains chloride, sulphate, carbonate, potassium, sodium and magnesium. Water-insoluble portion (23·1%) contains calcium, magnesium, iron and phosphate.

Preliminary chemical examination of the kernels.—The shell-free kernels were pulverised in a grinding machine and the product in 20 gm. lots was extracted with various organic solvents in a Soxhlet's apparatus. The solvents were subsequently evaporated. The results are indicated below:

Ether extract (0·61%).—Yellowish sticky substance.

Petroleum ether extract (0·38%).—Similar to the ether extract.

Benzene extract (1·04%).—Dark brown crystalline substance containing mainly alangol.

Alcohol extract (15·56%).—Dark reddish brown sticky substance containing embedded crystals of alangol. Contains sugars and tannins also.

Chloroform extract (3·35%).—Orange coloured sticky substance, partially solidifying to a crystalline mass on standing.

Ethyl acetate extract (2·46%).—Reddish brown crystalline solid containing mostly alangol together with some colouring matters.

Aqueous extract (31·31%).—Dark brown syrupy substance containing mostly tannins and sugars.

Isolation of alangol.—3·5 Kilos of the coarsely powdered kernels of seeds were extracted with boiling benzene in a five litre extraction flask fitted with a reflux condenser. The extraction was repeated with fresh benzene for a number of times until a small portion of the extract on complete evaporation did not give any crystalline residue. The combined extracts (10 litres) were distilled off to about one-tenth the original volume and allowed to cool, when large quantities of a brown crystalline substance were deposited. These were filtered off, washed with a little petroleum ether and dried in the steam oven when the substance became considerably reduced in volume, apparently due to the loss of benzene of crystallisation. Further quantities of the substance were obtained by evaporation of the mother liquors. The total amount of the crude material thus obtained from 7 kilos of the kernels yielded by 10 kilos of the whole seeds weighed 10·4 grams, thus giving an yield of 0·1 per cent. on the weight of the whole seeds. This was dark borwn in colour and melted indefinitely at 264–282° C. For purification, the substance was boiled under reflux for four hours with a 20% aqueous solution of caustic soda which removed most of the colouring and resinous matters. The residue was washed with hot water until free from alkali, dried and repeatedly crystallised from methyl alcohol with the addition of animal charcoal, when finally it was obtained in long colourless cotton-like needles meltimg at 296° C. The yield of the perfectly pure substance was 5·2 gm., thus giving an yield of 0·052 per cent. on the weight of the whole seeds.

Alangol crystallises best from 80 per cent. methyl alcohol in glistening needles with one molecule of water of crystallisation which is lost on heating the substance at 110° C. for two hours. It is sparingly soluble in cold methyl or ethyl alcohol, glacial acetic acid, benzene, chloroform and acetone, but dissolves more freely in these solvents in the hot state. In pyridine and nitrobenzene it dissolves very easily in the cold. The substance is almost insoluble in petroleum ether and is quite insoluble in water. In concentrated sulphuric acid in the cold it dissolves with a yellow colour which becomes reddish brown, specially on warming. The solution of the substance in acetic anhydride on treatment with chloroform and a few drops of concentrated sulphuric acid immediately assumes a pink colour which rapidly changes into violet, then blue and finally green. This is a characteristic reaction of all sterols. From concentrated sulphuric acid solution, the substance is

precipitated unchanged on dilution with water. (Found: C = 72·22, 72·13; H = 11·92, 11·62; M.W. by Rast's camphor method = 702; $C_{42}H_{84}O_7$ requires C = 72·0; H = 12·0; M.W. = 700.) $[\alpha]_D^{26°6}$ × 29·7° in chloroform.

Monoacetyl-alangol.—This was prepared in the usual manner by heating alangol with acetic anhydride and a few drops pyridine under reflux for one hour. The substance crystallises from dilute alcohol in colourless needles, which on heating shrink at 256° C. and melt at 265° C. (Found: C = 70·80; H = 11·72; $C_{44}H_{86}O_8$ requires C = 71·15; H = 11·59 per cent.)

Monobenzoyl-alangol.—This was prepared by heating under reflux a mixture of alangol (0·5 gm.), pyridine (20 c.c.) and benzoyl chloride (5 c.c.) for one hour. The product was poured into water and the colourless precipitate thus obtained was washed with water, dilute sodium carbonate solution and again with water. It was finally crystallised from dilute alcohol in colourless prisms melting at 276° C. (Found : C = 72·73; H = 11·35; $C_{49}H_{88}O_8$ requires C = 73·13; H = 10·94 per cent.)

Alangol-monophenylurethane.—This was prepared by allowing a mixture of alangol (0·5 gm.), phenylisocyanate (1 gm.) and dry benzene (200 c.c.) to stand at the ordinary temperature in a carefully closed flask for a week, when from the clear solution, a part of the phenylurethane derivative crystallised out. More of the substance was obtained by distilling off the solvent to one-tenth the original volume and allowing the mother liquor to crystallise during another week. The combined product was recrystallised from boiling alcohol in glistening prisms, melting at 242° C. (Found: N = 1·6; $C_{42}H_{83}O_6O.CONHC_6H_5$ requires N = 1·7 per cent.)

Alangol-digitonide.—This was prepared by heating under reflux a mixture of alangol (0·5 gm.) and digitonin (0·5 gm.) dissolved in alcohol (150 c.c.) for three hours. On cooling the digitonide crystallised out in glistening prisms melting at 270–273° C. (Found: C = 6·74; H = 9·80; $C_{42}H_{84}O_7.C_{55}H_{94}O_{28}$ requires C = 61·19; H = 9·35 per cent.)

Summary and Conclusion

1. From the kernels of the seeds of *Alangium Lamarki*, Thwaites, a sterol has been obtained crystallising in colourless silky needles and having a molecular formula $C_{42}H_{84}O_7$. This has been named "alangol".

2. The sterol has been found to contain an alcoholic hydroxy group, and a number of derivatives of this substance have been obtained.

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A NEW METHOD FOR THE DETERMINATION OF WATER IN ABSOLUTE ALCOHOL AND AN APPLICATION OF THIS METHOD IN STUDIES ON THE DRYING OF ALCOHOL

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Small quantities of water present in ethyl alcohol are usually estimated either by determining certain physical constants (such as density, viscosity, refractive index, etc.) or by actually determining the amount of water present in the alcohol by some analytical method.[1, 2, 3] Some of the physical methods are no doubt simple and fairly accurate; but the value of the physical constants are considerably affected by the other impurities that may be present in alcohol. The chemical methods are accurate and the small amounts of other impurities do not interfere; but the analytical processes involved are tedious. The method described in the present paper combines in a large measure the merits of the physical and the chemical methods. It is based on the principle that the solubility of an electrolyte (*e.g.*, sodium chloride) in alcohol is enhanced by the addition of water. The measurement of the electrical conductivity of the saturated solution of sodium chloride in any alcohol sample enables us to determine the water content of the sample.

The relative efficiencies of some of the more common methods of preparing absolute alcohol have been investigated by this method.

Experimental

Preparation of samples of "Absolute alcohol".—Four samples of absolute alcohol were prepared as follows :—Alcohol (from the distilleries of the Mysore Sugar Co., at Mandya) containing about 5% of water was refluxed for two hours with good quality quick-lime (about 30% of the wt. of alcohol) taking suitable precautions to exclude moisture. It was then distilled in an all-glass apparatus using an efficient spray-trap. After discarding about 100 c.c. of the distillate, the middle fraction (A) was carefully stored. A portion of the sample A was refluxed with calcium metal (filings)

for an hour and distilled as before in an all-glass outfit to get sample B. Sample C was prepared by distilling sample A over sodium. Sample D was obtained by distilling sample B once again over calcium.

Determination of electrical conductivity.—A stoppered bottle containing about 75 c.c. of alcohol sample and about 3 g. of sodium chloride (of reagent quality and dried at 140° C.) was left in a bath at about 60° C. for 20 minutes with frequent shakings. The bottle was then shaken for 10 minutes on a shaking machine. The temperature of the solution after shaking was usually found to be between 33 and 35° C. Then the bottle was left in an air-thermostat at 30° C. for a few hours until the solution attained the temperature of the thermostat. Thus a saturated solution of the salt was obtained. The saturated solution was quickly transferred to a bottle type conductivity cell with ground-in thermometer. The cell constant was 0·1204. The conductivity was measured by means of a Leeds and Northurp bridge with an extension coil. A microphone hummer was the source of current and a telephone was used as the null instrument. The electrodes were platinised. The resistance measured was about 150 to 470 ohms ; the capacity effects were found to be negligible, a practically perfect silence being obtained at the null point. It was noticed that during the transfer of the solution from the container to the conductivity cell, a small fall in temperature occurred. The temperature of the solution at the time of measurement was noted and a correction was applied for any small deviation of the temperature from 30° C. The values of the conductivities of the saturated solutions are given in Table I.

TABLE I

Specific conductivities of saturated solutions of sodium chloride in the samples of absolute alcohol

Sample	A	B	C	D
Specific conductivity in r. ohms $\times 10^4$	2·59	2·57	2·59	2·56

2. A few alcohol-water mixtures were prepared by adding known quantities of distilled water to a known weight of absolute alcohol. The water content of each mixture was calculated on the assumption that sample D was water free. The saturated solutions of these samples with sodium chloride were prepared and the conductivities determined. Results are given in Table II and Fig. 1. (This portion of the work was done in collaboration with Dr. K. S. Gururaja Doss.[4])

TABLE II

Water content of alcohol weight %	0	0·55	0·97	1·29	3·53	6·77
Specific conductivity in r. ohms $\times 10^4$ ..	2·56	2·85	3·17	3·44	5·29	8·74

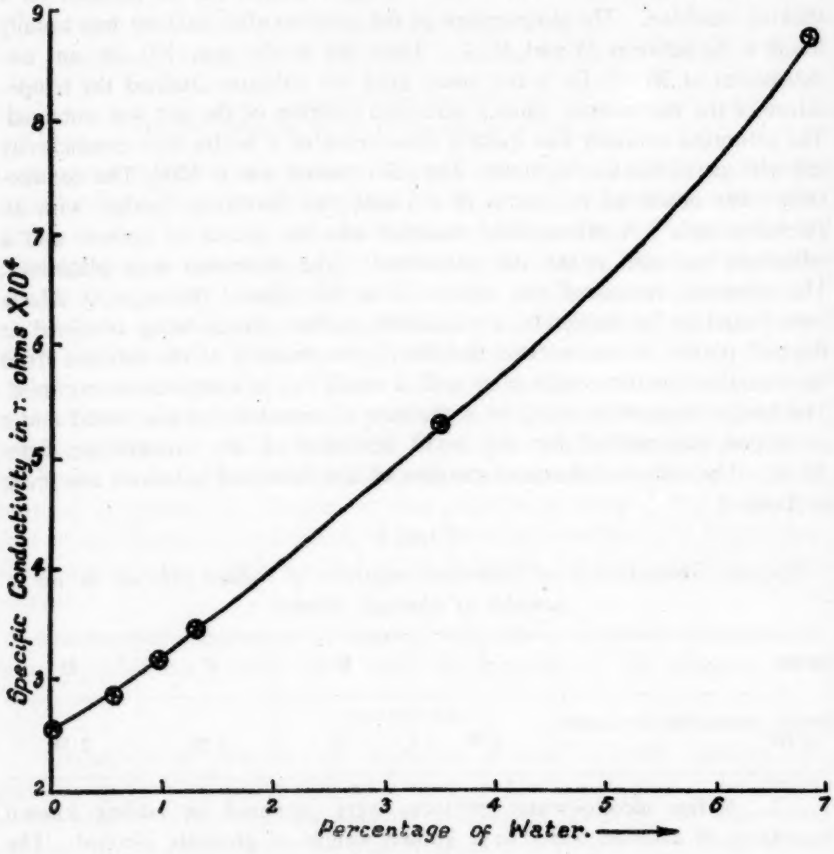

FIG. 1

Discussion

The results in Table I show that a good quality quick lime—the cheapest desiccant is very efficient in the preparation of absolute alcohol. The water

content of this sample of absolute alcohol does not differ from that of the best sample by more than 0·04%.

It is clear from Table II that this method of determining the water content of alcohol is capable of high precision. An accuracy of 0·3% in the determination of specific conductivity would correspond to 0·01% in the estimated water content. The method is simple since it is only necessary to prepare a saturated solution of sodium chloride in the sample under test and determine the specific conductivity of the solution. The water content can then be read off from the graph (Fig. 1). It may be pointed out that the method can conveniently be employed in distilleries in preference to the determination of density for estimating the water content of alcohol samples. In this connection it is of interest to note that the sodium chloride, is particularly well suited for the purpose since its solubility in alcohol does not change very much with temperature. According to the data of Kirn and Dunlap[5] the change in the solubility is about 0·4% per degree. A temperature control correct to 0·2° C. is therefore adequate for routine analysis. The values given in the present paper are sufficiently accurate to obtain the percentage of water with a maximum error of 0·04%. A sample of absolute alcohol was found from density measurements to have an alcohol content of 99·63 ±0·03%. The same sample by the new method gave a value of 99·58%.

Summary

A new method has been developed for the accurate determination of small quantities of water in ethyl alcohol, the method is based on the determination of electrical conductivity of a saturated solution of sodium chloride in the sample of alcohol. Owing to its simplicity and precision the method can conveniently be employed in routine analysis.

Quick-lime of good quality has been shown to yield absolute alcohol of very low water content.

In conclusion, I wish to record here my grateful thanks to Dr. K. S. Gururaja Doss and to Professor B. Sanjiva Rao for their keen interest in the work.

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REFLECTION OF LIGHT BY A PERIODICALLY STRATIFIED MEDIUM

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1. Introduction

The problem of the reflection of electromagnetic waves by a periodically stratified medium is of interest in many branches of physics, *e.g.*, the diffraction of X-rays by crystals and the scattering of light in solids and liquids. Although the theory of the phenomena has been elaborately investigated in the case of the reflection of X-rays by crystals, the optical analogues, which were known much earlier, have not been so thoroughly studied. The late Lord Rayleigh (1917) developed the theory of the reflection of light by a laminated structure, but he did not discuss its significance with regard to the spectral distribution of intensity in the reflected light. Recently, R. V. Subrahmanian (1941) has sought to rectify this omission and has computed the intensity distribution numerically from Rayleigh's formula in a number of cases.

In this paper an expression for the intensity of reflection from a stratified medium is derived in a very simple manner by a method somewhat similar to that employed by Darwin (1914) for the X-ray problem. A very general case is considered in which the medium is supposed to have a periodic structure, the nature of this being unspecified. The particular case of Rayleigh is then deduced from the general theory. The expressions so obtained are then discussed, having regard to the manner in which the functions appearing in it vary. This shows that it is not quite correct to say that the sharpness of the principal maxima increases in direct proportion to the number of stratifications, or that it is possible to deduce the number from the sharpness of the maxima, as has been assumed by various authors including the late Lord Rayleigh and R. W. Wood. It is found that the width of the primary maxima is not appreciably diminished by an increase in the number, except when the latter is small, and that the width is finite even when the number is infinite. This minimum width is found to depend only on the reflecting power of the stratifications. The discussion also

shows that there exist a number of secondary maxima in the interval between the principal maxima, and that they are asymmetrically distributed as regards their intensity on either side of a principal maximum.

2. *Derivation of the Fundamental Formulæ*

We shall consider a non-absorbing medium in which there is a periodic variation of optical properties. Let O_1, O_2, O_3,.... O_{n+1} be consecutive points in the medium at which the properties of the medium are identical. Then the distances O_1O_2, O_2O_3,.... O_nO_{n+1} are all identical, and each is equal to the thickness of the stratification. It is supposed that there are n such stratifications.

Since there are variations in the optical properties, it is evident that there will be a large number of multiple reflections ; and consequently, there will be two streams of energy in the medium, one passing upwards, and the other downwards. Let T_1, R_1 ; T_2, R_2 ; etc., represent the electric vectors in the upward and downward streams of energy at the points O_1, O_2, etc., respectively.

According to our notation, T_1 is the amplitude of the incident wave, and let θ_1 be the angle made by T_1 with the common normal to the stratifications. Then, at each of the points O_2, O_3, etc., the two streams of energy will make the same angle θ_1 with the common normal. We shall now denote by r and t the complex reflection and transmission coefficients for a single stratification, on which light is incident at the angle under consideration. Here again, we refer the vibration to points O_1, O_2, etc., that is, t is the ratio of the electric vector in the transmitted wave at O_{s+1} to that at O_s, and r is the ratio of the reflected wave at O_s to that at O_s in the incident wave.

With these definitions, we see that R_s consists of two parts : (1) due to the transmission of $R_{s+1} = tR_{s+1}$ and (2) due to the reflection of $T_s = rT_s$. Hence,

$$R_s = rT_s + tR_{s+1} \tag{1}$$

Similarly, $$T_s = tT_{s-1} + rR_s \tag{2}$$

Our aim is now to find the amplitude T_{n+1} of the wave transmitted by the last stratification, and of that reflected out of the first, *viz.*, R_1. For this, eliminating the R's and the T's successively from (1) and (2), we get

$$T_{s-1} = \frac{1 + t^2 - r^2}{t} T_s - T_{s+1} \tag{3}$$

$$R_{s-1} = \frac{1 + t^2 - r^2}{t} R_s - R_{s+1} \tag{4}$$

For convenience, call the factor $\frac{1+t^2-r^2}{t}$ as y. It is evident that $R_{n+1}=O$, since no light is incident from below. From (4), therefore

$$R_{n-1}=yR_n$$

Now, applying relation (4) successively, we get

$$R_{n-2}=yR_{n-1}-R_n=(y^2-1)\,R_n, \text{ etc., giving}$$

$$R_1=\left[y^{n-1}-\frac{(n-2)}{\underline{1}}\,y^{n-3}+\frac{(n-4)\,(n-3)}{\underline{2}}\,y^{n-5}-\ldots\right]R_n=J_n(y)\,R_n \text{ (say)}$$

$$\text{Then } \frac{R_1}{R_n}=f_n(y) \tag{5}$$

Again, putting $s=(n+1)$ and $R_{n+1}=O$ in (2),

$$T_n=T_{n+1}/t$$

Applying relation (3) successively,

$$T_{n-1}=yT_n-T_{n+1}=(y/t-1)\,T_{n+1}, \text{ etc., giving}$$

$$T_1=\left[\frac{1}{t}\,f_n(y)-f_{n-1}(y)\right]T_{n+1} \text{ or}$$

$$\frac{T_1}{T_{n+1}}=\frac{1}{t}f_n(y)-f_{n-1}(y) \tag{6}$$

Also, from relation (1), since $R_{n+1}=O$, $R_n=rT_n$ giving

$$R_n=\frac{r}{t}\,T_{n+1}, \text{ and from (5), we get}$$

$$\frac{R_1}{T_{n+1}}=\frac{r}{t}f_n(y) \tag{7}$$

We have thus evaluated both T_{n+1} and R_1 in terms of T_1. Now, the series appearing as $f_n(y)$ is well known, and is summable. Putting $y=2\cosh\beta$, we have, in fact, (Jolley, 1925)

$$J_n(y)=f_n(2\cosh\beta)=\frac{\sinh n\beta}{\sinh\beta}.$$

Also, the right-hand side of equations (6) and (7) can both be expressed in terms of hyperbolic functions by writing

$$\frac{r}{\sinh\beta}=\frac{t}{\sinh\alpha}=\frac{1}{K}.$$

(7) goes over into the form $\frac{R_1}{T_{n+1}}=\frac{\sinh n\beta}{\sinh\alpha}$. (8)

We may evaluate K using the relation $\cosh \beta = (1 + t^2 - r^2)/2t$, and obtain $K = \sinh(\alpha + \beta)$. Hence,

$$\frac{r}{\sinh \beta} = \frac{t}{\sinh \alpha} = \frac{1}{\sinh(\alpha + \beta)} \tag{9}$$

and

$$\frac{T_1}{T_{n+1}} = \frac{1}{t} f_n(y) - f_{n-1}(y) = \frac{\sinh(\alpha + n\beta)}{\sinh \alpha} \tag{10}$$

Finally,

$$\frac{R_1}{\sinh n\beta} = \frac{T_{n+1}}{\sinh \alpha} = \frac{T_1}{\sinh(\alpha + n\beta)}. \tag{11}$$

The angles α and β can be expressed in terms of r and t. We have seen that

$$\cosh \beta = \frac{1 + t^2 - r^2}{2t}. \tag{12}$$

$$\text{Similarly } \cosh \alpha = \frac{1 - t^2 + r^2}{2r}. \tag{13}$$

From these, it follows at once that

$$\sinh^2 \alpha = \frac{\{(r+t)^2 - 1\}\{(r-t)^2 - 1\}}{4r^2} \tag{14}$$

$$\sinh^2 \beta = \frac{\{(r+t)^2 - 1\}\{(r-t)^2 - 1\}}{4t^2} \tag{15}$$

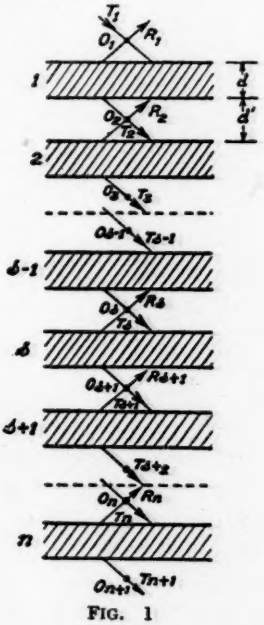

FIG. 1

So far, our theory has been quite general. We shall now consider a case treated by Lord Rayleigh, one in which the stratification consists of a set of n parallel plates, each of thickness d and of refractive index μ separated by empty gaps of thickness d'. Let the rays make an angle θ_2 with the common normal in the space within the plates and an angle θ_1 in the space between. For shortness, let us write the path retardations $2\mu d \cos\theta_2$ and $2d\cos\theta_1$ within the plates and in the spaces between, respectively, as δ and δ'. Also let η be the reflecting power of the surfaces of separation between the two media. Then, referring by O_1, O_2, etc., to the points bisecting the intervals between the plates, we can show from the electromagnetic theory of light that

$$r = \frac{-\eta\,(e^{ik\delta}-1)}{(e^{ik\delta}-\eta^2)\,e^{\frac{1}{2}ik\delta'}}\;;\quad t = \frac{(1-\eta^2)\,e^{\frac{1}{2}ik\delta}}{(e^{ik\delta}-\eta^2)\,e^{\frac{1}{2}ik\delta'}} \tag{16}$$

where $k = 2\pi/\lambda$.

Substituting these values, we get

$$\sinh^2\alpha = \frac{\{\cos^2\tfrac{1}{4}k(\delta+\delta')-\eta^2\cos^2\tfrac{1}{4}k(\delta-\delta')\}\{\sin^2\tfrac{1}{4}k(\delta+\delta')-\eta^2\sin^2\tfrac{1}{4}k(\delta-\delta')\}}{\eta^2\sin^2\tfrac{1}{2}k\delta} \tag{17}$$

$$\sinh^2\beta = \frac{-4}{(1-\eta^2)^2}\{\cos^2\tfrac{1}{4}k(\delta+\delta')-\eta^2\cos^2\tfrac{1}{4}k(\delta-\delta')\}\{\sin^2\tfrac{1}{4}k(\delta+\delta') - \eta^2\sin^2\tfrac{1}{4}k(\delta-\delta')\} \tag{18}$$

Since we shall have often to make use of these relations, we put $\frac{1}{4}k(\delta+\delta') = \phi$ and $(\delta-\delta')/(\delta+\delta') = c$, and rewrite them in a simpler form as

$$\sinh^2\alpha = \frac{\{(\cos^2\phi-\eta^2\cos^2 c\phi)\,(\sin^2\phi-\eta^2\sin^2 c\phi)\}}{\eta^2\sin^2(1+c)\,\phi} \tag{19}$$

$$\sinh^2\beta = \frac{-4}{(1-\eta^2)^2}\{\cos^2\phi-\eta^2\cos^2 c\phi\}\{\sin^2\phi-\eta^2\sin^2 c\phi\} \tag{20}$$

3. *The Two Cases*

We are now in a position to consider the intensity of the reflected beam. We need discuss only the reflected part, since the transmitted part will exhibit the complementary phenomena. Since r and t are complex, we should expect R_1 also to be complex, so that the intensity is represented by $|R_1|^2$. Let us now represent the ratio of the intensity $|R_1|^2$ of the reflected beam to that T_1^2 of the incident beam by R, which we may call the

"reflecting power" of the stratified medium. Then

$$R = \frac{\sinh^2 n\beta}{\sinh^2 (\alpha + n\beta)}, \tag{21}$$

where $\sinh^2 \alpha$ and $\sinh^2 \beta$ have the values given in (19) and (20).

Before proceeding further, it is important to note that both α and β are complex. Hence, we write $\alpha = \alpha_1 + i\alpha_2$ and $\beta = \beta_1 + i\beta_2$, where α_1, β_1, α_2, β_2 are real. A consideration of equations (19) and (20) will show that $\sinh^2 \alpha$ may have positive or negative values, and that $\sinh^2 \beta$ will correspondingly have negative or positive values. Hence we must distinguish two distinct cases:

(i) $\sinh^2 \alpha$ is $-$ve, and consequently $\sinh^2 \beta$ is $+$ ve. In this case $\sinh \alpha$ is imaginary and $\sinh \beta$ is real, so that α is pure imaginary $= i\alpha_2$ and β is real $= \beta_1$. Hence,

$$\frac{T_1}{R_1} = \cosh \alpha + \sinh \alpha \coth n\beta = \cos \alpha_2 + i \sin \alpha_2 \coth n\beta_1.$$

Therefore, $$\frac{1}{R} = \left|\frac{T_1}{R_1}\right|^2 = 1 + \frac{\sin^2 \alpha_2}{\sinh^2 n\beta_1}. \tag{22}$$

As β_1 is finite, $\sinh^2 n\beta_1$ steadily increases with n tending to the value ∞ as $n \to \infty$. Hence, for a particular value of α and β, R steadily increases with n, and $\to 1$ as $n \to \infty$.

(ii) $\sinh^2 \alpha$ is $+$ve and $\sinh^2 \beta$ is $-$ve, making $\alpha = \alpha_1$, and $\beta = i\beta_2$. This gives

$$\frac{1}{R} = 1 + \frac{\sinh^2 \alpha_1}{\sin^2 n\beta_2} \tag{23}$$

so that R fluctuates between O and a maximum as n is increased.

We may now consider the conditions under which these cases occur. From (19) and (20), it is easily seen that case (i) occurs when η^2 lies between

(*a*) $\dfrac{\cos^2 \phi}{\cos^2 c\phi}$ and (*b*) $\dfrac{\sin^2 \phi}{\sin^2 c\phi}$, and that case (ii)

occurs when it lies beyond these limits.

It is easy to see that if one of the two quantities (*a*) or (*b*) is less than unity, the other is greater. But η^2 has a range of values only between O and 1. Hence, the conditions of occurrence of the two cases may be rewritten as below :—

Case (i) occurs if $\eta^2 >$ either (*a*) or (*b*) whichever is < 1, and

case (ii) occurs if $\eta^2 <$ either (*a*) or (*b*) whichever is < 1.

4. *The Principal Maxima*

We shall now consider the nature of the reflection. At the very outset, we note that the rays from the corresponding parts in each stratification will reinforce each other, if the path retardation $\delta + \delta' = s\lambda$, where s is an integer. It then follows that the reflecting power R of the n plates must be a maximum, $R_{max.}$ for these values of λ. We shall call these maxima as the " primary maxima ". In this case, $k(\delta + \delta') = 2\pi s$ and $\phi = s\pi/2$, which gives

$$\sinh^2 \alpha = \eta^2 \cos^2 \tfrac{1}{2}k\delta - 1 \qquad (24)$$

Since η and $\cos \frac{1}{2}k\delta$ are always < 1, $\sinh^2 \alpha$ is always negative. This corresponds to case (i), R steadily increasing with n to the limiting value 1, as $n \to \infty$.

Now, this phenomenon of a steady increase of R with n can occur, as we have seen, only if η^2 is $> \dfrac{\sin^2 \phi}{\sin^2 c\phi}$ or $\dfrac{\cos^2 \phi}{\cos^2 c\phi}$, whichever is less than unity. Let us therefore find the solutions of the equations

$$\sin^2 \phi = \eta^2 \sin^2 c\phi \qquad .. \quad (A)$$

$$\cos^2 \phi = \eta^2 \cos^2 c\phi \qquad .. \quad (B)$$

This is easily done graphically. Fig. (2) shows the curves $y = \cos \phi$; $y = \pm \eta \cos c\phi$ and $y = \sin \phi$; $y = \pm \eta \sin c\phi$, drawn for two sets of

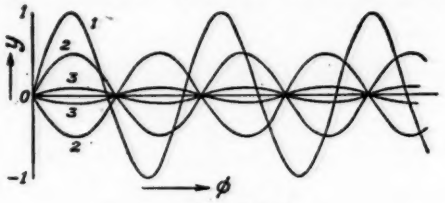

FIG. 2 *(a)*

1. $y = \sin \phi$ 2. $y = \pm \cdot 5 \sin \cdot 9\phi$ 3. $y = \pm \cdot 1 \sin \cdot 9\phi$

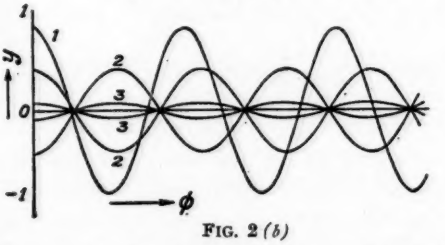

FIG. 2 *(b)*

1. $y = \cos \phi$ 2. $y = \pm \cdot 5 \cos \cdot 9\phi$ 3. $y = \pm \cdot 1 \cos \cdot 9\phi$

values of $\eta = \cdot 5$ and $\cdot 1$ and for $c = \cdot 9$. We see from these that, in general, the solutions of the equations (A) and (B), which are given by the

values of ϕ corresponding to the intersection of the two curves, always occur in pairs on either side of $\phi = s\pi/2$. The pairs of solutions of A and B occur alternately. Let us call the two solutions on either side of $s\pi/2$ as ϕ_1 and ϕ_2.

5. *The Subsidiary Maxima*

It is easily seen that for values of ϕ situated in those intervals between ϕ_1 and ϕ_2 which contain $s\pi/2$, case (i) holds and the reflection steadily increases with n. Let us now consider the other region of values of ϕ. In this region, it is evident that case (ii) holds, so that

$$\frac{1}{R} = 1 + \frac{\sinh^2 \alpha_1}{\sin^2 n\beta_2}. \tag{22}$$

Taking the expression (20) for $\sinh^2 \beta$, it is easily seen that $\sinh^2 \beta = 0$, for the values of ϕ corresponding to the solutions of A and B and that it is negative in the region between, reaching a maximum negative value somewhere between. Hence, $|\beta_2|$ must also increase from O to a maximum, which is less than $\pi/2$ and then decrease to O. Then, if n is sufficiently large, $\sin^2 n\beta_2$ must undergo fluctuations between O and 1, and consequently, R also must fluctuate between zero and a maximum in this range. This gives rise to subsidiary maxima in the region between the primary maxima.

It is also easily seen that for the same range of values of β_2, the fluctuations increase in number as n is increased, so that the number of secondary maxima, and consequently, their sharpness increase as n increases.

Coming now to the intensity of the secondary maxima, it is influenced only by the values of $\sinh^2 \alpha_1$ since $\sin^2 n\beta_2 = 1$, for every one of them. Therefore, the secondary maxima must all lie on a curve whose equation is

$$\frac{1}{R} = 1 + \sinh^2 \alpha_1. \tag{25}$$

The general form of this curve is shown in Fig. 3 for a typical value of c and of η. It may be noted that, in general, there is a marked asymmetry in the intensity of the secondary maxima about a primary maximum.

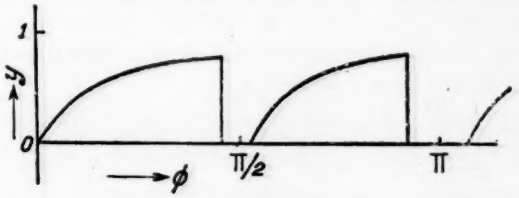

FIG. 3

6. *The Width of the Primary Maxima*

We have already seen that in those regions between the solutions of A and B which contain $s\pi/2$, the intensity steadily increases with n, and that, in the other regions, it fluctuates with n. Now for a particular value of n, we note that, on passing out from the former region to the latter, the intensity becomes zero for values of ϕ corresponding to the first subsidiary minimum on either side. Thus, the width of a primary maximum is given by the distance between the first subsidiary minima on either side of $s\pi/2$.

Now, the first subsidiary minimum occurs for that value of ϕ for which $n\beta_2 = \pi$. Also, we know that β_2 increases from the value O at $\phi = \phi_1$ or ϕ_2 to a maximum and then diminishes. Hence, the larger the value of n the smaller will be the range of values of ϕ, outside $\phi_1\phi_2$ in which R falls to zero. Hence, as n increases, the width of the primary maximum must decrease.

However, it is easily seen that the width cannot go on diminishing indefinitely, since R can never be equal to zero in the range of values of ϕ from ϕ_1 to ϕ_2. Hence, the minimum width is given by the distance $\phi_1\phi_2$. We call this the " limiting width " for any order of primary maximum. We then see that, as n increases, the width steadily decreases, until at a fairly high value of n, it is very nearly equal to the limiting width. After this, the width does not undergo any appreciable diminution, however much n is increased.

7. *Variation of the Primary Maxima with Other Factors*

We shall now see how the intensity and width of the primary maxima vary with other factors when n is a constant.

Variation with η.

We have already seen that for the primary maxima

$$\sinh^2 \alpha = \eta^2 \cos^2 \tfrac{1}{2}k\delta - 1 = \{\eta^2 \cos^2 (1 + c)\, s\pi/2\} - 1 \qquad (26)$$

In the same way, $\sinh^2 \beta$ reduces to

$$\sinh^2 \beta = \frac{4\eta^2}{(1-\eta^2)^2} (\cos^2 cs\pi/2)\,(1 - \eta^2 \sin^2 cs\pi/2) \qquad (27)$$

Since, in this case, $\sinh^2 \alpha = (i \sin \alpha_2)^2$, we see from (26) that $\sin \alpha_2$ decreases as n increases. Also, from (27), we see that $\sinh^2 \beta_1 = \sinh^2 \beta$ increases, making β_1 and consequently $\sinh^2 n\beta_1$ increase. Hence, from relation (22) we find that R increases as η increases.

At the same time, as increase in η produces an increase in the limiting width as may be inferred from the curves in Fig. 2.

Variation with μ.

Let us suppose that the refractive index of the intervening medium is increased. Then μ is diminished, resulting in a decrease in the value of η.

The intensity of the primary maximum is diminished and its limiting width is also diminished.

Variation with Obliquity and the State of Polarization

Both these factors affect only the value of η and the effect is easily predictable. If the beam is polarised with the electric vector in the plane of incidence, the reflection coefficient η_1 is equal to unity at angle of incidence 90°, which rapidly diminishes with θ_1 to $\eta_1 = O$, at $\theta_1 = \tan^{-1}\mu$, the Brewsterian angle. As θ_1 is further diminished, η_1 rises to a small value. $R_{max.}$ also must show similar variation with θ_1.

If, however, the beam is polarised with the electric vector perpendicular to the plane of incidence, the reflection coefficient η_2 is equal to unity at $\theta_1 = 90°$ and slowly decreases to the same value as η_1 at $\theta_1 = O$. Hence, R steadily diminishes as θ_1 diminishes.

Corresponding to the variations in η, we must also expect a variation in the limiting width of the primary maxima as the angle of incidence is varied.

8. *A Particular Case*

It can be seen from Fig. 2 that the limiting width of the primary maxima varies in general, from order to order. However, for a special case, when $\delta = \delta'$, this is the same for all orders. We shall now consider this case in detail. Here, since $\delta = \delta'$, $c = O$, and the equations A and B reduce to

$$\cos^2\phi = \eta^2 \cos^2 c\phi = \eta^2 \quad .. \quad (A') \text{ and}$$

$$\sin^2\phi = \eta^2 \sin^2 c\phi = O \quad .. \quad (B')$$

the solutions of which are $\phi = s\pi$ and $\phi = s\pi \pm \cos^{-1}\eta$. We see that both the solutions of (B') coincide at $s\pi$, so that we can have no principal maximum at $\phi = s\pi$. Hence, only odd orders of principal maxima exist in this case. This can also be explained physically, since for an even order, $\delta + \delta' = 2s\lambda$, and since $\delta = \delta'$, each is $= s\lambda$. Now the alternate reflecting surfaces are dissimilar, and therefore produce a relative phase change of π or path retardation of $\lambda/2$, so that the beams from each pair of consecutive surfaces destructively interfere, and completely annul each other, and there will be no reflection for that particular order. Also, for every one of these odd orders of reflection, we have from (25) $\sin^2\alpha_2 = 1$, and from (26) $\sinh^2\beta_1 = \dfrac{4\eta^2}{(1-\eta^2)^2}$, which is a constant independent of s. Hence, from (22) we see that the intensity of the primary maxima is the same for all orders. The limiting width also is given by $2\sin^{-1}\eta$, which is the same for all orders, and the maximum possible for a given η.

Again, taking the secondary maximum curve, $1/R = 1 + \sinh^2\alpha_1$, we get in this particular case.

$$\sinh^2 \alpha = \frac{(\cos^2 \phi - \eta^2 \cos^2 c\phi)\,(\sin^2 \phi - \eta^2 \sin^2 c\phi)}{\eta^2 \sin^2 (1+c)\,\phi}$$

$$= \frac{\cos^2 \phi}{\eta^2} - 1, \text{ so that}$$

$$\frac{1}{R} = \frac{\cos^2 \phi}{\eta^2}, \text{ and } R = \frac{\eta^2}{\cos^2 \phi}. \tag{28}$$

This is symmetrical about $\phi = (2s+1)\,\pi/2$, so that the secondary maxima are symmetrical about the primary maxima. Also R for these subsidiary maxima may have a value $= 1$ at $\phi = \cos^{-1} \pm \eta$, and it decreases to a value η^2, at $\phi = s\pi$, midway between the primary maxima. Thus the secondary maxima may have considerable intensities in the immediate neighbourhood of the primaries, and *may even have an intensity greater than them.*

9. *Stratifications of Vanishing Thickness*

Let us suppose that one of the media is very thin, *e.g.*, let δ' be very small compared with δ. In this case, $c = \dfrac{\delta - \delta'}{\delta + \delta'}$ will be very nearly equal to unity. Let it be $= 1 - x$, where x is very small. Then we may put $\sin xs\pi/2 = xs\pi/2$ and $\cos xs\pi/2 = 1$, approximately, so that the values of $\sinh^2 \alpha$ and $\sinh^2 \beta$ become

$$\sinh^2 \alpha = -\sin^2 \alpha_2 = -(1 - \eta^2) \tag{29}$$

$$\text{and } \sinh^2 \beta = \sinh^2 \beta_1 = \frac{4\eta^2}{(1-\eta^2)^2} \left(\frac{xs\pi}{2}\right)^2 \tag{30}$$

for the sth order. From these, it is easily seen that if $\delta' = 0$, then $x = 0$, and $\sinh^2 \beta_1 = 0$, making the reflection $R = 0$. This is obvious, for the condition $\delta' = 0$ means that there is no second medium, and no reflections can occur in this case.

Also, from (30) we see that if x increases, $\sinh^2 \beta$ also increases with it, and from (22), it follows that R also increases. Thus, when the thickness of one of the layers is small, the intensity of the primary maxima is a direct function of the thickness.

A more detailed analysis, involving no approximations, shows that the intensity actually fluctuates as x is increased to larger values. The value of x is $2\delta'/(\delta + \delta')$, and an increase in x means an increase of δ' relative to δ. It is found that as x increases from 0 to $1/s$, the intensity of the sth order increases from zero to a maximum. Then it decreases to zero at $x = 2/s$. Thereafter, it undergoes fluctuations, having maximum values if $x = (2m+1)/s$, and zero values if $x = 2m/s$, where m is an integer. Although it is not possible to vary x in any specimen and observe these fluctuations, this discussion is of interest because it enables us to arrive at

a rough idea of the relative thicknesses of the two layers by means of a study of the relative intensities of the various orders of primary maxima. Thus, if $\delta = \delta'$, $x = \frac{1}{2}$, and all even orders must vanish, as we have already seen. If $\delta = 2\delta'$, $x = \frac{1}{3}$, and the 3rd, 6th, etc., orders vanish, and so on.

10. *Graphical Illustration*

In order to illustrate the preceding discussion, a particular case has been numerically computed, and the results are shown in Fig. 4. Here,

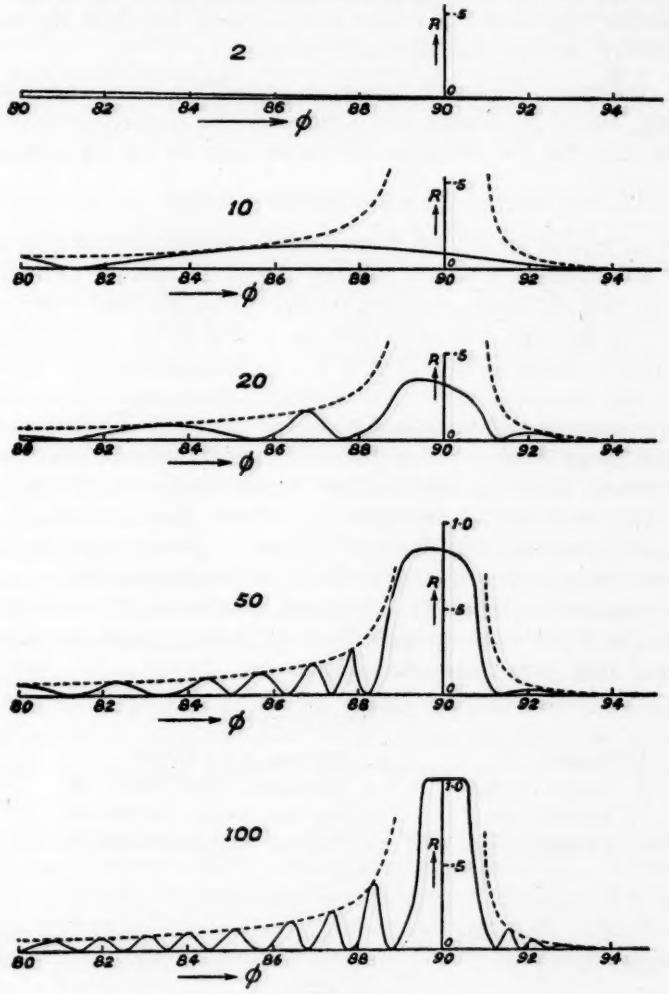

FIG. 4

the reflecting power η is supposed to be 0·1, and the value of c, 0·9. The spectral distribution of intensity in the neighbourhood of the first order principal maximum has been drawn for 2, 10, 20, 50 and 100 plates. The curves show the way in which the principal maximum is built up as the number of plates is increased. They also show that, when the number is increased above 20, the diminution in width is small.

The dotted line marks the curve on which the secondary maxima lie, and it shows how the intensity of these are widely different on either side of the principal maximum. It is also interesting to note how the number of the secondary maxima increases as n increases.

In conclusion, the author wishes to express his sincere gratitude to his professor, Sir C. V. Raman, for suggesting the method of attacking the problem, and also for the deep interest he took in the investigation.

11. *Summary*

An expression for the reflection from a medium consisting of n stratifications is derived in a simple manner, utilising Darwin's method in the analogous case of X-rays, modified to suit the optical case. The particular case of Lord Rayleigh is deduced from the general theory, and the expression so obtained is discussed in a general way by a consideration of the manner in which the functions vary. An important result that comes out of this is that the sharpness of the principal maxima cannot be indefinitely increased by increasing the number of stratifications, but that the width has a minimum limiting value, which depends only on the reflecting power of the stratifications. The mathematical discussion also shows that there exist a number of secondary maxima in the interval between the primary maxima, and that, in general, these show a marked difference in their intensities on either side of a principal maximum. Particular cases, when the paths in the two media are equal, and also when the path in one of them is small, are also investigated, and they yield some interesting results.

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A NEW FLUORESCENCE REACTION FOR THE DETECTION OF BORIC ACID

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The detection of boric acid and borates in admixture with inorganic substances has always been a problem of considerable difficulty. New reagents and procedures have been suggested from time to time but all of them suffer from one or other defect so that no satisfactory reagent is available at present.

The turmeric test described by Trömmsdorff[1] as early as 1815 is highly sensitive, but it is interfered with by the oxidising agents,[2-6] such as hydrogen peroxide, chromate, chlorate, nitrite, arsenate and ferricyanide ; iodides and fluorides also interfere but only to a lesser degree. Consequently elaborate procedures[2,3,5,11] have been described to eliminate or reduce these interfering radicles so that the test might be employed successfully.

The commonly employed alkyl borate test is also rendered uncertain in presence of chlorides and copper[7,10] for the former leads to the formation of alkyl halides which burn with a green edged flame and the latter itself colours the flame green. Further Krauss[8] has shown that barium also interferes with this test on account of the volatility of the $BaSO_4$, H_2SO_4 compound. Even phosphoric acid has been shown to interfere with this test. It is interesting to note in this connection that the use of glycerol[10] in place of sulphuric acid minimises the interference by copper and chloride considerably.

The boron trifluoride test[11] also suffers from similar disadvantages ; it cannot be carried out in test-tubes made of boro-silicate glass, and copper and barium interfere with the test in the same way as they do with the alkyl borate test.

Recently many hydroxy-anthraquinones and their derivatives have been introduced by Feigl and others as reagents for the detection of boric acid. These give intensely coloured solutions in concentrated sulphuric acid which show characteristic colour changes in presence of boric acid. From this group of compounds, alizarin-S, purpurin and quinalizarin have been suggested by

Feigl and Krumholz[12] and rufianic acid by Rosenthaler.[13] The naphthalene derivative, chromotrope-2B, has been suggested by Komarovsky and Poluektov.[14] Though all these are highly sensitive, fluorides and oxidising agents interfere so that their removal is essential for the success of the test. The elimination of fluorides as recommended by Komarovsky and Poluektov (*loc. cit.*) and adopted by Feigl, consists in heating the substance with silica and concentrated sulphuric acid till fumes of sulphur trioxide appear; a procedure which obviously involves loss of boric acid.[15]

Various other tests described in literature are of limited applicability. Mention may be made of the tests employing Congo-red,[16] Methyl red or Sofnol-indicator No. 1,[17] Carob seed gum[18] and Carmine red.[19] An interesting reaction[20] is the rose-pink to blood red colour given by a tincture of mimosa flowers by means of which boric acid can be detected in presence of chloride, iodide, nitrate and sulphate. The test is, however, interfered with by organic acids and sodium phosphate.

Phosphorescence and fluorescence effects obtained with boric acid have also been employed for its detection. The phosphorescence with fluorescein as an activator has been suggested by Zhirov.[21] A fluorescence reaction with tincture cochineal has been described by Szebellady and Gaal[22]; this, however, is interfered with by several metals.

In a previous communication,[23] it has been reported that boric acid yields with resacetophenone dissolved in concentrated sulphuric acid a brilliant blue fluorescence visible under Cenco Black Light Source and this fact can be utilised for the detection of boric acid on a semi-micro scale. This reaction has now been investigated further to determine its applicability in qualitative analysis and the results obtained are reported below.

Experimental

A. With Concentrated Sulphuric Acid.—

Interference by Basic and Acidic Radicles.—A preliminary investigation has been carried out with all the basic radicles and several of the acidic radicles included by Caven in *Systematic Qualitative Analysis* (1934).

The method of testing adopted was as follows.—

Resacetophenone (10 mg.) was dissolved in concentrated sulphuric acid (10 c.c.) and the solution divided into two equal parts. To one part placed in a quartz test-tube was added 1·0 mg. of boric acid and 100 mg. of the sodium or potassium salt of the acidic radicle under investigation. For the basic radicle the metallic borates were used; where these were not available, an easily soluble salt of the metal along with 1·0 mg. of boric acid was

employed. If the solution could not be effected in the cold, the salt was at first brought into solution in concentrated sulphuric acid with warming and the solution cooled before use. The second part of the resacetophenone solution was placed in another quartz test-tube of approximately the same dimensions and was used for preparing the appropriate blank in each case. After thorough mixing the test-tubes were placed under the Cenco Black Light Source inside a darkened cabinet and observations made. All the tests were carried out in the cold.

Basic Radicles.—None of the basic radicles examined gave any fluorescence in the absence of boric acid. In testing for boric acid also there was no interference and in all cases a brilliant blue fluorescence was obtained. Under the conditions of testing, the interference which might be expected due to the colour of the metal ion in the case of copper, nickel, cobalt and chromium was also found to be absent.

Acidic Radicles.—None of the sodium and potassium salts of the acid radicles examined gave any fluorescence in the blank test. In testing for boric acid, however, there was complete interference from nitrate and fluoride and no fluorescence was noticeable. With thiosulphate there was precipitation of sulphur but this did not interfere with the observation of fluorescence. Chlorate, chromate and ferricyanide oxidised the reagent producing coloured solutions in which, however, the blue fluorescence was visible. In the case of bromide and iodide, the separation of the halogen besides bromination of the reagent in the former case made it difficult to observe the fluorescence. Tartrate interfered to some extent by undergoing carbonisation; this difficulty was reduced by diluting the solution with sulphuric acid.

In view of the fact that several of the common acidic radicles interfered in this method, the following were not examined:—nitrite, hypochlorite, cyanide, sulphocyanide, cyanate, bromate, iodate, the per-acids, peroxide, manganate, phosphite, hypophosphite and silicofluoride. In all other cases a brilliant blue fluorescence was observed with boric acid.

Limits of Identification and Sensitiveness.—

Reagents: (1) *Boric Acid.*—A solution containing 10 mg. of boric acid per c.c. was prepared from an A.R. quality sample by dissoliving in concentrated sulphuric acid. A series of solutions containing 1·0, 0·1, 0·01.... mg. per c.c. was prepared by diluting the above solution with concentrated sulphuric acid.

(2) *Resacetophenone.*—Pure resacetophenone (0·25 g.) was dissolved in 100 c.c. of concentrated sulphuric acid.

Method.—1 c.c. of the boric acid solution was placed in a quartz test-tube, treated with 3 c.c. of the reascetophenone solution and the volume made up to 10 c.c. with concentrated sulphuric acid. To facilitate this operation the test-tube was roughly graduated at the 10 c.c. mark. After mixing the tube was placed under the lamp and the following observations made:—

TABLE I

No.	Boric acid mg. per c.c.	Observations
1	10·0	Brilliant blue fluorescence
2	1·0	Blue fluorescence—easily visible
3	0·1	Very pale blue fluorescence—visible
4	0·01	Not easily visible

Limit of Identification = 100 γ

Limit of Sensitiveness = 1 : 10,000.

B. With Phosphoric Acid.—

Since in the above experiments using concentrated sulphuric acid interference occurred with several acidic radicles, experiments were performed with phosphoric acid in the place of this acid. In the first place it was found that the boric acid—resacetophenone reaction occurred in the presence of syrupy phosphoric acid yielding a blue fluorescence visible under the lamp and identical with that obtained with sulphuric acid. Secondly, it was found that the number of interfering acidic radicles was considerably less when phosphoric acid was used. Consequently a detailed investigation was carried out using this acid.

Interference by Basic and Acidic Radicles.—In addition to the basic radicles which were examined with concentrated suphuric acid the following were also included:—Beryllium, Lanthanum, Thorium, Zirconium, Tungsten, Vanadium, Cerium, Uranium, Titanium and Molybdenum. All the acidic radicles previously examined were investigated and the list was extended to include nitrite, bromate, iodate, perchlorate, periodate, persulphate, sulphocyanide, cyanate, and peroxide (hydrogen peroxide).

The method of testing adopted was similar to that previously described except that the salt was dissolved in dilute acetic acid whenever possible or a dilute nitric or hydrochloric acid solution of the salt was treated with acetic acid and used. Solid resacetophenone (10 mg.) was dissolved in this solution and to it was added an equal volume of syrupy phosphoric acid.

Basic Radicles.—None of the basic radicles examined interfered with the blue fluorescence obtained with boric acid. Though precipitation of phosphates occurred in many cases, the precipitates dissolved in excess of phosphoric acid. The colours of the solutions in the case of copper (pale blue), nickel (pale green) and chromium (green) were not visible under the lamp so that there was no interference from them and any fluorescence present could be readily detected. In a few cases, however, though there was no interference with the test, certain peculiarities were observed and these are given in the table below:—

TABLE II

Solution	Observation	Remarks
1. *Vanadium*— Vanadium pentoxide was dissolved in hot dilute nitric acid.	A pale yellow solution resulted; with phosphoric acid a deep blue ring was obtained; on shaking the soultion became dirty greenish blue. Blue fluorescence easily observed.	The colour of the solution did not interfere with the test.
2. *Cerium*— (*a*) Cerous sulphate dissolved in warm dilute nitric acid.	At first clear colourless solution with bright blue fluorescence. It turned gradually pink to deep red solution masking the fluorescence.	There is no interference immediately after mixing the solution. Interference occurs on standing probably due to ceric ions.
(*b*) Ceric sulphate dissolved in dilute nitric acid.	Deep yellow solution with bright blue fluorescence; gradually turns deep red the fluorescence being masked.	Interference occurs only on standing.
3. *Uranyl acetate*— Dissolved in water.	Pale yellow solution. Bright blue fluorescence.	Very dilute aqueous solutions of uranyl acetate exhibit green fluorescence in day light, which, however, disappears on addition of acetic acid.
4. *Uranium trioxide*— Dissolved in dilute nitric acid	Bright blue fluorescence. Slight reddish colour developed on standing.	No fluorescence in the blank.

Acidic Radicles.—Among the acidic radicles which interfered in the sulphuric acid method, it was found, that bromide, iodide, nitrate and tartrate no longer interfered. With fluoride, however, there was complete interfence as in the method using sulphuric acid. With perchlorate, persulphate, periodate and cyanate the solution was colourless and there was no interference. Thiosulphate yielded a turbid solution due to separation of sulphur, but this did not interfere with the fluorescence. With other acid radicles, however, certain peculiarities were observed and these are reported below:

TABLE III

Radicle in solution	Observation	Remarks
1. Chromate	Pale yellow solution at first ; turned reddish and finally deep red. Blue fluorescence.	Carbonisation of the reagent occurred and this rendered observation of fluorescence difficult.
2. Nitrite	The solution, on addition of phosphoric acid, quickly turned deep cherry red ; fluorescence could not be observed. Repeated with a small amount of nitrite.—Blue fluorescence.	Development of colour is probably due to the interaction of nitrous acid with the resacetophenone.
3. Chlorate	At first colourless solution exhibiting blue fluorescence ; solution gradually developed yellow colour.	Except for the colour developed there is no interference.
4. Bromate	Solution at first deep yellow ; decolourised on shaking. No fluorescence.	The deep yellow colour is due to the liberation of bromine. The negative reaction is probably due to bromination of resacetophenone.
5. Iodate	Yellow colour developed. Blue fluorescence.	No interference.
6. Ferricyanide	Solution yellow. Blue fluorescence.	Do.
7. Sulphocyanide ..	Do.	Do.

Limits of Identification and Sensitiveness.—

Reagents (1) *Boric Acid Solution.*—A series of aqueous solutions containing 1·0, 0·1, 0·01.....mg. of boric acid per c.c. was prepared.

(2) *Resacetophenone Solution.*—Pure resacetophenone (0·25 g.) was dissolved in 100 c.c. of dilute acetic acid.

Method.—The method adopted was similar to that used previously with sulphuric acid. In making up the solution to 10 c.c., however, syrupy phosphoric acid was used.

TABLE IV

Boric acid (mg. per c.c.)	Observation
1·0	Deep blue fluorescence
0·1	Blue fluorescence—easily visible
0·01	Pale blue fluorescence
0·001	Very pale blue fluorescence—just visible
0·0001	No fluorescence

Limit of Identification = 1 γ

Limit of Sensitiveness = 1 : 1,000,000.

Limit Proportions.—In order to throw light on the scope of the reaction, experiments were performed to determine the approximate quantities of the various acidic and basic radicles in the presence of which a definite amount of boric acid (0.1 mg.) can be detected by the phosphoric acid method.

Solutions.—Solutions of various acidic and basic radicles containing about 10 mg. of the radicle per c.c. were prepared using soluble salts. These solutions were then diluted with water suitably for getting the lower concentrations.

(2) *A solution containing* 0·1 mg. of boric acid per c.c. was used.

(3) A 0·25 per cent. solution of resacetophenone in dilute acetic acid was used.

Method.—1 c.c. of the boric acid solution was placed in a quartz test-tube, treated with 1 c. c. of the test solution followed by 3 c.c. of the resacetophenone solution and finally the volume was made up to 10 c.c. with syrupy phosphoric aicid. After mixing, observations were made under the lamp. If the fluorescence was not easily visible, the next lower concentration of the test solution was employed until it could be detected without difficulty. The results obtained were approximate and no attempt was made to determine the exact magnitudes of the " limit proportions " in view of the limitations imposed by the lamp.

TABLE V

No.	Radicle	Limit proportions in mg. with (0·1 mg. of boric acid)	No.	Radicle	Limit proportions in mg. (with 0·1 mg. of boric acid)
1	Copper	60·0	7	Chromate ..	2·0
2	Cobalt	10·0	8	Chlorate	10·0
3	Chromium ..	10·0	9	Nitrite	4·0
4	Nickel	30·0	10	Iodate	20·0
5	Ferricyanide ..	10·0	11	Fluoride (KHF_2) ..	4·0
6	Bromate	2·0			

From the above data it is evident that bromate and chromate interfere most with the test while nitrite and fluoride come next in order. It is interesting to note that the interference by fluoride which was found to be complete in the previous experiments is only partial, it being possible to detect easily as little as 0·1 mg. of boric acid in presence of 40 times its weight of the fluoride ion. The interference by nitrite is of no serious consequence as the radicle could readily be eliminated by means of dilute acids.

A noteworthy feature of the above data is that relatively large amounts of coloured cations do not interfere with the test.

Discussion

The resacetophenone—sulphuric acid method for the detection of boric acid suffers from several defects. Sulphuric acid being an oxidising agent liberates the halogens from bromides and iodides and these interfere with the test on account of their colour. Further free bromine interferes with the reaction by brominating the resacetophenone. In this connection it may be pointed out that the introduction of bromine into a hydroxy-ketone has a considerable bathofloric effect as has been shown in a previous communication.[23] The complete interference by nitrate in this method is evidently due to nitration of the reagent (*loc. cit*). In the case of fluoride the complete interference observed could be readily explained as due to the formation of the complex fluoborate ions. Oxidising agents such as chromate, chlorate and ferricyanide obviously interfere by oxidising the reagent itself producing deeply coloured solutions which render observation of the fluorescence difficult. In the case of tartrate carbonisation is the cause of interference. In addition the viscosity of the solutions renders the test less sensitive.

The substitution of sulphuric acid by syrupy phosphoric acid, however, obviates several of the defects observed in the above case. The acid radicles which interfere are chromate, bromate, nitrite and fluoride. With bromate, the interference can be explained as due to bromination of the reagent. To explain the formation of bromine under the experimental conditions it is suggested that the bromate either contained a trace of bromide or a small amount of the latter was produced by reduction and that the mixture of bromate and bromide in presence of the strong acid yielded bromine. Chromate interfered by oxidising the reagent and producing coloured solutions. The interference of nitrite, however, is due to the formation of a deep red colour by the interaction of nitrous acid with the reagent. Attention may also be drawn to the fact that the interference by fluoride is only partial and that the fluorescence with boric acid is observed in presence of as much as forty times its weight of the fluoride ion.

A comparison of the limits of identification and sensitiveness of the reactions carried out with the above acids shows that the method using phosphoric acid is one hundred times more sensitive than that using sulphuric acid. While with sulphuric acid 100γ is the limit of identification, with phosphoric acid the limit is 1γ so that the latter method is serviceable for the detection of micro quantities of boric acid. It may be also pointed out

that the number of acid radicles which interfere in the phosphoric acid method is comparatively small and these with the exception of the fluoride can be readily eliminated.

The sensitiveness of the resacetophenone—phosphoric acid method compares favourably with various reactions which have been suggested in the literature as shown in the table below:—

TABLE VI

Test	Limit of Identification (Boric Acid)	Method of Testing
1. Resacetophenone—Phosphoric acid ..	1·0 γ	Macro-method
2. Turmeric[9,11]	1·0 γ	Do.
	0·1 γ	Do.
3. Tincture of Mimosa Flowers[20]	0·4 γ	Do.
4. Phosphorescence[21]	20·0 γ	Do.
5. Boron Trifluoride[11]	0·1 γ	Do.
6. Alkyl Borate[24,25]	200·0 γ	Do.
	2·0 to 7·0 γ	Micro-method
7. Tincture cochineal[23]	12·0 γ	Macro-method
	0·5 γ	Micro-method
8. Alizarin-S[3]	5·5 γ	Spot test
9. Purpurin[2]	3·3 γ	Do.
10. Quinalizarin[2]	0·33 γ	Do.
11. Chromotrope—2B[3]	0·44 γ	Do.

Further several of these tests suffer from interference by many acidic and basic radicles (*vide infra*) while in the resacetophenone-phosphoric acid method the interference is much less; none of the basic radicles interferes and the acid radicles that do so are few in number and these with the exception of fluoride can be easily eliminated.

The results obtained for limit proportions indicate that the reaction is quite serviceable for the detection of boric acid in qualitative analysis. It may also be pointed out that resacetophenone is readily prepared and easily purified.

Summary

A new fluorescence reaction for the detection of boric acid with resacetophenone and phosphoric acid has been described. None of the metallic radicles examined interferes while among the acid radicles chromate, bromate, chlorate, nitrite and fluoride do so to a limited extent. The reaction compares favourably with those described in the literature both as regards limit of identification and also interference. It has been shown that the test is applicable for the detection of micro-quantities of boric acid.

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